

# GLYCERIN

## *Its Industrial and Commercial Applications*

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## PREFACE

THIS BOOK, which is based on a comprehensive survey of recent patent literature and reported research findings, is designed to present a digested and indicative review of actual and potential glycerin uses in a variety of industrial fields.

With this in mind, no effort has been made to discuss at length the technical methods of glycerin production as such, but only the physical and chemical properties of this product have been described in reference to its industrial and commercial utilization. The recovery of glycerin from soap lyes and other crudes, the various processes for the production of glycerin by fermentation, and so on, have been covered exhaustively in other books. It seems unnecessary to review them here.

Much of the material included in this book has been taken from articles by the authors which have appeared in various trade and technical publications and from papers presented at professional and scientific gatherings.

In certain of the cited formulae, where no method of preparation is given, it is assumed that this is obvious from the constituents of the formula itself.

The authors desire to express their appreciation to Mr. Allan P. Ames for his advice and suggestions in the preparation of the book.





## FOREWORD

WHEN I read or hear the word glycerin mentioned, I frequently recall C. F. Kettering's now famous story of the two young men friends of his who steadfastly refused to divulge the nature of a very mysterious piece of research occupying all of their attention. Finally, in a moment of weakness, the two lads revealed to him that they were seeking a universal solvent.

"But," said the practical-minded head of General Motors' research, "what will you keep it in if you do find it?"

Glycerin definitely is not the mythical solvent of Kettering's amusing yarn and I am certain that not even such ardent glycerin enthusiasts as Georgia Leffingwell and Milton Lesser would claim such occult power for the product which they have done so much to popularize.

However, few chemicals serve the chemist and the manufacturer in so many and in such varied ways; few present a greater challenge to the imagination and the ingenuity of the researcher. In war and in peace, tremendous quantities are consumed each year in the manufacture of such widely diversified products as explosives, metals, foods, beverages and cosmetics to mention but a few and not necessarily the most important ones. Every man, woman or child comes in daily contact with glycerin, directly or indirectly. It is a most useful servant of mankind in health and in sickness; it helps to beautify and clean our homes. Many of the familiar household products we depend upon contain glycerin or its derivatives.

The valuable contributions of the authors have appeared from time to time in American scientific, technical and trade journals. They have followed the work of others painstakingly and have accumulated a wealth of information which they have disseminated freely to industry. I feel honored and privileged to have been able to assist them in a small way by publishing first in Chemical Industries and later in Chemical and Engineering News, several of their informative articles. I, along with others, repeatedly have urged upon Dr. Leffingwell and Mr. Lesser, the desirability

of publishing in book form a detailed dissertation of the industrial and commercial applications of glycerin. Wisely they have prepared a practical treatise which will provide research chemists, manufacturers, plant operators, industrial workers and students with comprehensive data presented in a clear and simple style.

Incorporation of hundreds of proven formulae adds immeasurably to the industrial value of the book and provides the stimulus for other scientific workers to expand still further the frontiers of "the sweet principle of fats" discovered by the celebrated Swedish chemist, Scheele, one hundred and sixty-six years ago.

WALTER J. MURPHY, Editor  
Industrial and Engineering Chemistry;  
Chemical and Engineering News;  
Director, American Chemical Society  
News Service.

# TABLE OF CONTENTS

CHAPTER		PAGE
	PREFACE . . . . .	iii
	FOREWORD . . . . .	v
I	BRIEF HISTORY OF GLYCERIN . . . . .	1
II	ADHESIVES AND CEMENTS . . . . .	8
	Glues, pastes, glycerin-litharge cements, adhesive tapes, Cellophane adhesives, etc.	
III	CLEANERS AND POLISHES . . . . .	15
	Glass, metals, floors, furniture; abrasive polishes, wetting agents and detergents, etc.	
IV	ELECTRICAL EQUIPMENT . . . . .	23
	Electrolytes, electroplating, insulations, electrolytic condensers, cements and binders, etc.	
V	EXPLOSIVES . . . . .	31
	Nitroglycerin, dynamite, cordite, etc.	
VI	LEATHER . . . . .	36
	Softening agents, tanning preparations, hide depilatories, dressings and polishes, fur treatments, leather substitutes, etc.	
VII	LUBRICANTS . . . . .	42
	High-pressure lubricants, greases, explosionproof, low-temperature, solvent-resistant, etc.	
VIII	METALS . . . . .	50
	Quenching and tempering media, electroplating solutions, galvanizing protective finishes, rust-removers, foundry cores, soldering fluids, etc.	
IX	PACKAGING MATERIALS . . . . .	58
	Cellophane, sealing and capping compounds, bottle caps and bands, sealing materials, cork compositions, etc.	

CHAPTER		PAGE
X	PAPER . . . . .	65
	Vulcanizing medium, lubricant, softening agent, solvents, proofings, rubber substitutes, etc.	
XI	PHOTOGRAPHY . . . . .	71
	Films and emulsions, color processes, mountants, "stay flat" solutions, projector screens, etc.	
XII	PLASTICS . . . . .	81
	Cast alkyds, melamines, acrolites, glue-glycerin, etc.	
XIII	PRINTING AND LITHOGRAPHY . . . . .	88
	Printing rollers, inks, hectographs, decalcomania, silk-screen, etc.	
XIV	PAINTS AND PROTECTIVE COATINGS . . . . .	95
	Alkyd resins as protective coatings, insulating paints, etc.	
XV	RUBBER . . . . .	99
	Vulcanizing medium, lubricant, softening agent, solventproofings, rubber substitutes, etc.	
XVI	TEXTILES AND DYES . . . . .	105
	Rayon and other artificial fibers, printing pastes and dye compositions, lubricants, etc.	
XVII	TOBACCO . . . . .	112
	Hygroscopic agent, flavor solvent, etc.	
XVIII	GLASS . . . . .	119
	Glass-etching processes, glass-marking inks, glass- protective coatings, etc.	
XIX	AGRICULTURE . . . . .	124
	Seed treatments, plant-growth preparations, animal preparations, sheep dips, tree-wound treatments, insecticides, pest baits, etc.	
XX	COSMETICS . . . . .	131
	Lotions, creams, manicure products, hair prepara- tions, deodorants, depilatories, eye preparations, hand preparations, liquid rouges and powders, shaving preparations, etc.	

# Table of Contents

ix

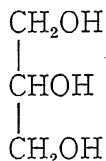
CHAPTER		PAGE
XXI	BEVERAGES . . . . .	140
	Base flavors for soft drinks, extracts, and syrups, foaming compounds, smoothing agent for alcoholic beverages, coloring preparations, etc.	
XXII	FOODS . . . . .	149
	Confectionery, sweetening agent, flavoring prepa- rations, vanilla and other extracts, dairy products, shortenings, baked goods, rapid-freeze refrigerant, etc.	
XXIII	MEDICINE AND SURGERY . . . . .	157
	Antiseptics, wound dressings and bandages, instru- ment lubricants, adhesive tapes, suppositories, burn treatments, etc.	
XXIV	ORTHODONTIA AND DENTISTRY . . . . .	164
	Toothpastes, mouth washes and gargles, anti- septics, disclosing solutions, impression materials, polishing agents, etc.	
XXV	PHARMACEUTICALS . . . . .	176
	Tinctures and solutions, ointments, pastes and jellies, capsules, biologicals, drug extraction, liquid vehicles, glycerites, etc.	
XXVI	VETERINARY MEDICINE . . . . .	183
	Animal biologicals, antiseptics, wound treatments, dermal parasitocides, dressings, etc.	
XXVII	OPTOMETRY . . . . .	192
	Abrasives for lenses, spectacle cleaners, pencils for goggles, eye lotions, etc.	
XXVIII	GLYCERIN DERIVATIVES . . . . .	198
XXIX	LIST OF GLYCERIN USES . . . . .	211
XXX	APPENDIX . . . . .	243
	INDEX . . . . .	49



## CHAPTER I

### BRIEF HISTORY OF GLYCERIN

GLYCERIN is a clear, colorless syrupy, almost odorless liquid with a slightly sweet taste. Its name is derived from the Greek word "glykeros," meaning sweet. Chemists refer to it as a trihydric alcohol having the structural formula:



Glycerin was first discovered in 1779 by Karl Wilhelm Scheele, a young Swedish chemist. A druggist in a little country town, he worked under a constant handicap of poverty and debt, without even ordinary laboratory conveniences, and unaware himself that he was doing the most significant chemical pioneering of his epoch.

When he extracted "the sweet principle of fats" from olive oil, neither Scheele nor his generation suspected the full importance of the achievement. They could not guess that in a highly industrialized future, this product, under the name of glycerin, would develop into a thing of a thousand uses: in therapeutics, food processing, cosmetics, and scores of industries.

In 1936, on the one hundred and ninety fourth birthday of the discoverer, fifteen outstanding American scientific and industrial organizations united in a formal cable to Crown Prince Gustaf Adolf of Sweden expressing appreciation of Scheele's services to mankind. They described the isolation of glycerin as a "significant contribution to modern life."

It was altogether fitting that the tribute should come from the United States. It was in the new land across the ocean that the application of what was long known as "Scheele's sweet principle"

was later to find its widest field of usefulness. It was here, with the phenomenal growth of American industry, that the vast potentialities of glycerin were to reach their greatest development.

After extracting glycerin from olive oil, Scheele had drawn it from almond oil, lard and butter, thus confirming its presence in both animal and vegetable fats and oils. In a sense, he was duplicating a process of nature, since glycerin, as the Journal of the American Medical Association (May 20, 1933) pointed out, is a "normal digestion product." Glycerin is also formed naturally in the process of wine fermentation.

In the ordinary course of eating and drinking, all of us get indirectly a daily supply of the substance somewhere along the line: so many simple, homely items of consumption contain glycerin; milk, for example, and butter, cheese, salad oils, lard, vegetable shortenings, cocoanut products, nut meats, etc. Experts have even calculated that with an edible fat consumption in the United States of about seven billion pounds annually, our population automatically absorbs in the natural process of digestion some 700 million pounds of glycerin, aside from glycerin consumed in other food products and beverages.

These facts give dramatic emphasis to the elementary consideration that glycerin is literally a product of nature: the farm, plantation, forest and ocean, with all that this implies in terms of natural purity and wholesomeness. It is in effect one of the natural resources of the countryside, since it may be derived from all growing things, both vegetable and animal.

Sugar, too, is an important source of glycerin, through fermentation. In 1858, Pasteur found that approximately one-thirtieth of the sugar, transformed under ordinary circumstances in the fermentation of grape juice and similar liquors into alcohol and other substances, becomes converted into glycerin.

The bulk of the world's supply of glycerin, however, is obtained from the saponification of the oils and fats known as glycerides. The first United States patent for the recovery of glycerin and salts from spent soap lyes by distillation was issued in 1870. Other important advances soon followed, paving the way for the modern processes. Itself a natural product, glycerin is refined and purified by concentration, filtration, and distillation until it emerges as one of the purest, most wholesome, as well as



most useful ingredients known to the medical, pharmaceutical, and chemical professions.

The variations of the modern saponification processes, by which glycerin is recovered commercially from fats, may be described briefly as follows: (1) by combining the fat with an alkali, thus releasing the glycerin; (2) by low-pressure hydrolysis with the aid of a catalyst; (3) by high-pressure hydrolysis in a digester, either with or without a catalytic agent. The first process is commercially the most important, producing soap and glycerin. The other two processes produce fatty acids and glycerin.

The crude glycerin yield from the first process is designated as "80% soap lye crude." The glycerin yield from the other two processes is designated as "88% saponification crude." The purification of either type of crude glycerin involves distillation of glycerin at low pressures and treatment with decolorizing carbon. Refined glycerin is sold in four principal grades: \*

Chemically Pure or U.S.P.	A high grade, water-white glycerin meeting the requirements of the United States Pharmacopoeia, suitable for use in foods, pharmaceuticals, cosmetics or for any purpose where the highest quality is demanded. It has a specific gravity of 1.249– 25/25°C.
High Gravity	A pale yellow glycerin for industrial purposes, with a specific gravity of 1.262– 15.5/15.5°C.
Dynamite	A yellow glycerin made especially for the explosives. It has a specific gravity of 1.262– 15.5/15.5°C.
Yellow Distilled	A yellow glycerin for industrial purposes, with a specific gravity of 1.259– 15.5/15.5°C.

One of the most outstanding properties of glycerin, making it essential in a vast number of uses, is its power to absorb and retain moisture from the air. Under certain conditions, it can absorb up to 50% of its own weight in water. This makes it uniquely valuable in processing where moisture content must be maintained, or where it is desirable to avoid excess drying.

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\* For further information and recommendations as to the grade of glycerin best suited to a specific industrial application, it is suggested that the purchaser consults his supplier.

Glycerin also possesses remarkable solvent powers which make it useful for a wide variety of industrial and pharmaceutical purposes. Many substances, such as iodine, bromine, tannin, alkaloids, thymol, phenol, mercuric chloride, boric acids, fixed alkalis, etc., are more soluble in glycerin than in water. Glycerin thus makes possible the preparation of highly concentrated solutions of such substances. The solvent powers of glycerin are much used in the extraction of many drugs, such as pepsin and endocrine-gland substances. Other uses, based on solvent powers, include the production of practically all cosmetics; perfumes, flavoring extracts, printing inks and polishes, and textile dyeing. "There are some dyes which do not go into true solution," reports one textile chemist. "Where these are used, glycerin is necessary as a dispersing agent."

That glycerin is itself insoluble in ether, chloroform, and gasoline further adds to its value.

Because glycerin is non-corrosive, it does not affect metals. It is very stable, with a high boiling point ( $290^{\circ}\text{C}.$ ), which resists evaporation, and a low melting point ( $17^{\circ}\text{C}.$ ). It does not turn rancid and has a definite preservative action in the preparations of which it is a constituent. In pharmacy and medicine, it is extensively used as a preservative for vaccines and allergic extracts. Again, in food processing, such as preserves, meat extracts, cream mixtures, it acts to retard fermentation and mold. These antiseptic and preservative powers are probably due to the hygroscopic action by which it deprives the organisms of water and causes dehydration of the bacteria. In the tanning and finishing of leather, glycerin enters into many steps of the procedure, displaying to the best advantage its preservative action as a hygroscopic agent to make and keep the leather soft and pliable. The rubber industry finds it invaluable to keep rubber goods from drying out and becoming brittle. Adhesives of every description utilize its moisture-retaining and preservative action.

The *viscous character* of glycerin and the fact that it prevents other products from drying and hardening when exposed to the air, fits it for many mechanical uses in lubricants: in automatic shock absorbers; big guns, hydraulics; shaft lubrication of collieries; pistons of air compressors; mechanical refrigeration;

delicate machinery; clock mechanisms and meters. In a recent series of tests to determine relative ability of lubricants to reduce corrosion indentations of ball and roller bearings in automobiles, glycerin, which was included with a large variety of oils and greases, ranked among the first twenty. In places where oil cannot be used with best results, glycerin is especially valuable either as a lubricant in itself or as a constituent of special lubricants, for example, in the processing and pumping of gasoline where oil lubricants have been found to dissolve too quickly.

The viscosity of glycerin, together with its clarity and lack of color, adapt it ideally for use in liquid preparations that need increased body or thickening, or in essences, syrups, and liquors.

Glycerin, being both a primary and a secondary alcohol, reacts to produce a variety of ethers and esters which are finding considerable use in commerce. It is also a weak acid and as such may be utilized to form a number of salts of the alkali earths, and heavy metals which have a diversity of actual and potential applications. Currently, the increasing realization of the possibilities of the glycerin derivatives suggests still wider industrial scope for glycerin.

In the manufacture of synthetic plastics and resins, millions of pounds of glycerin are annually consumed. One reason for the extensive use of these resins lies in the fact that, depending upon the modifiers used, almost any conceivable type of product may be produced, ranging from liquids to solids and from non-drying through semi-drying to air-drying types as well as baked-type finishes. Their durability is attested by their wide-spread use for enamels in the automobile and refrigerator industries. A novel application was revealed in the announcement that the copper roof of one of the New York World's Fair buildings was coated with an alkyd resin which prevented discoloration.

The chemistry of these resins is not fully understood, but it is generally assumed that following an initial simple esterification of glycerin and phthalic anhydride, interesterification and polymerization occur, resulting in the formation of very large molecules. In the presence of fatty acid modifiers, even more complicated interesterification takes place. Such reactions are only possible with polyhydric alcohols such as glycerin. This field is so

highly specialized that space does not permit further discussion here in spite of its importance. For a complete survey of this field the reader is referred to "Synthetic Resins and Plastics." \*\*

As a natural product, glycerin has been scientifically proved to be entirely safe for human use not only externally on any part of the body but internally in medicines and foods. It was in commenting on published studies of glycerin as a food, that the *Journal of American Medical Association* † alluded to the substance as a "normal digestion product." This wholesomeness is a vital consideration in connection with the growing use of glycerin not only in commercial food processing but also in the manufacture of any products which may come into close and continuous contact with the human skin.

In view of the wide range of properties of this versatile compound, no satisfactory substitute has ever been found to replace glycerin in all its extensive applications. No other single product, natural or synthetic, combines all the attributes of glycerin.

Glycerin finds applications in almost every branch of modern industry because it presents a combination of desirable properties not to be found in any other substances. In some industrial processes, it may be employed because it imparts one or two of its important characteristics to the finished products but, in the main, it is used because it affords a variety of requisite qualities.

The average person knows glycerin only in its most elementary form, whether on the kitchen shelf, on the cosmetic table, or in the medicine chest. He is but vaguely aware, if at all, that it is an essential though invisible ingredient in endless items of everyday use or consumption; or that it enters importantly into a large number of technical and industrial processes.

The uses to which the product lends itself are so varied, indeed, that it is difficult to find a major industry which does not owe some debt to glycerin. Chemists and technical directors, faced with problems in developing new products or improving old ones, as a matter of course, consider the properties of glycerin in finding a solution.

It is natural, therefore, that the demand for the product has

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\*\* Carleton Ellis, *Synthetic Resins and Plastics*, New York, Reinhold Publishing Corp., 1923.

† *J. Am. Med. Assoc.*, 100, 1604 (1933).

grown consistently, particularly in the last two decades. Especially in this country, with its highly developed industry and its constant emphasis on safety and efficiency, both consumption and production have more than doubled in recent years.

## CHAPTER II

# ADHESIVES AND CEMENTS

IN AN average, normal year, approximately two and one-half million pounds of glycerin go into the manufacture of adhesives. The makers and users of adhesives, especially adhesives of the water-soluble type, have come to know that there is really no complete substitute for glycerin in products that meet modern packaging requirements.

Technicians and users alike will agree that glycerin is the best softener or plasticizer for many bonding agents. In government-sponsored publications<sup>1, 2</sup> on adhesives for the graphic arts, standards for softeners used in "glues" are based upon the characteristics of glycerin. Through its hygroscopic action, this fluid has the property of absorbing moisture from the atmosphere and of retaining a portion of the essential moisture when the relative humidity of the surrounding air is low. Concurrently, glycerin imparts flexibility to the compositions in which it is used by retaining an appreciable amount of moisture under changing atmospheric conditions. The big difference between its boiling point and freezing point helps to assure efficient action under a wide range of climatic conditions. This has always been an important consideration in a country with as varied a climate as ours and it becomes increasingly important as American materials find their way to every corner of the globe.

In their discussion of adhesives, Strong and Tator<sup>3</sup> remark that most of the water-soluble adhesive bases, particularly glue, dry to give very hard, stiff and in most cases, brittle films. Hence, it is usually desirable to impart some flexibility to these adhesives, especially when they are to be employed for the bonding of flexible surfaces or where bonded rigid surfaces may be subjected to considerable shearing force. Water-soluble organic liquids, such as glycerin, are commonly used for this purpose.

Acting as both a hygroscopic and as a plasticizing or flexibilizing agent, and possessing certain penetrating and "wetting"

## *Adhesives and Cements*

properties of its own, glycerin helps to produce a more continuous, longer-lasting bond, one that will dry smoothly and yet retain sufficient moisture. The factor of safety inherent in glycerin also favors its use. Completely non-toxic in itself, glycerin does not evaporate to produce noxious or fire-hazard fumes. From this, it becomes evident why glycerin should find use in connection with such varied adhesive bases as animal glues, casein, starches and starch derivatives, silicates, rubber dispersions, vinyl resins and other compounds used to make direct application bonding materials, "remoistening" adhesives, and selfadhering pressure films.

Glycerin starts early as an ingredient of adhesives in packaging materials, since it finds frequent employment in the production of paper containers and cartons. One quite recent patent,<sup>4</sup> describes methods for preparing adhesives suitable for making laminated containers of paper or other materials. The adhesives, which, it is claimed, remain pliable and flexible indefinitely, are formed from casein, triethanolamine or urea, glycerin as a plasticizer, and sufficient water to give the desired workability.

There are many other interesting examples of utility of glycerin in adhesives for making containers. The following flexible, non-warp glue is for use in making better grade boxes, as given in Bennett's <sup>5</sup> standard reference text:

	Parts by Weight
Low Grade Gelatin .....	30.0
Glycerin .....	10.0
Glucose .....	25.0
Phenol .....	0.4
Water .....	34.6

The same source provides another typical flexible paper box glue consisting of:

	Parts by Weight
Animal Glue .....	45
Glycerin .....	15
Water .....	39
Preservative .....	1

Label adhesives, of both the direct application and re-moistening type, find glycerin a frequent and standard component.<sup>6</sup> Thus, a rather fluid label gum can be made from: <sup>5</sup>

	Parts by Weight
Gum Arabic .....	30.0
Saturated Lime Water .....	15.0
Glycerin .....	1.0
Water .....	54.0

If a more viscous product is desired, the following formula should serve:

	Parts by Weight
Gum Arabic .....	35.0
Aluminum Sulfate (Crystals) .....	2.0
Glycerin .....	2.0
Water .....	61.0

Where specific adhesive requisites must be met, the qualities inherent in glycerin are frequently called into play in the formulation of bonding agents for securing paper to glass, metallic surfaces, lithographed surfaces or the like. Both the technical and patent literature offer numerous examples of the use of glycerin in adhesives for bonding paper to glass. Rather typical is the following paper-to-glass adhesive:<sup>5</sup>

	Parts by Weight
Cassava or Tapioca Flour .....	12.5
Zinc Chloride .....	2.0
Glycerin .....	10.0
Water .....	150.0

Of course, other starches or flour can be used in place of the cassava or tapioca, but the products obtained are not of such high quality.

Another patented adhesive suitable for securing paper to glass, metals and similar materials consists simply of:<sup>7</sup>

	Parts by Weight
Glue .....	100.0
Glycerin .....	400.0
Calcium Chloride .....	37.0

The problem of securing good adhesion between metal surfaces and paper is one that has been efficiently overcome by the use of several compositions of which glycerin is an integral part. There



are formulas for glycerin in adhesives for tin<sup>8</sup> and for many other similar uses. The following, taken from standard texts,<sup>5</sup> is recommended for securing adhesion to tin cans:

	Parts by Weight
Gum Arabic .....	50.0
Glycerin .....	10.0
Liquid Antimony Chloride .....	2.0
Water .....	90.0

When it is desired to apply an already gummed label to metal surfaces, moistening with the following solution<sup>5</sup> will result in a good bond:

	Parts by Weight
Acetic Acid .....	8.0
Glycerin .....	2.0
Water .....	6.0

Nowadays when already lithographed cans or containers have to be used for purposes other than those originally intended, suitable adhesives greatly facilitate the attaching of new labels. Glycerin, now readily available, has proved to be preeminently suitable for such adhesives. One example of an adhesive for use on oiled or inked surfaces employs glycerin as a plasticizer for an aqueous rubber dispersion containing casein.<sup>9</sup> Bennett's reference text offers the following paste for attaching labels to lithographed cans:

Flour .....	$\frac{1}{2}$ lb.
Water .....	2 pt.
Glycerin .....	1 oz.
Nitric Acid .....	2 dr.
Methyl Salicylate .....	$\frac{1}{2}$ dr.

In the preparation of remoistening adhesives, as exemplified by gummed tapes, prepared labels, envelopes and such, the drying time, curling tendency, tackiness, viscosity and many other factors require careful control.<sup>10</sup> Glycerin is useful in such preparations, especially so in preventing excessive brittleness of the dried adhesive film and in combating the tendency of the prepared paper to curl.

## 12    *Glycerin—Its Industrial and Commercial Applications*

Gum arabic formerly had been much used in preparing these remoistening adhesives and glycerin was widely used as the plasticizing agent.<sup>11</sup> Today, the emphasis appears to be on dextrin gums and related starch-conversion products. Here, too, glycerin is valued as a plasticizer and hygroscopic agent. This is quite apparent in at least half a dozen patents<sup>12</sup> granted to Bauer and his associates for making remoistening adhesives suitable for use on paper.

It is well known that glycerin is an important raw material in the manufacture of Cellophane films where it serves as the major plasticizer to maintain flexibility and strength. Indeed during the 1940–41 period, approximately 14.2% of all glycerin produced in this country was consumed by the Cellophane industry.

It is, therefore, not surprising that the characteristics which make glycerin so useful in Cellophane proper should also find extensive utility in the adhesives required for this popular packaging substance. For example, one simple adhesive for Cellophane that has often been recommended<sup>5, 13</sup> with minor variations consists simply of:

	Parts by Weight
Gum Arabic .....	17.5
Water .....	52.5
Glycerin .....	30.0
Formaldehyde .....	0.05

Patented adhesives, such as one<sup>14</sup> based on the use of rubber dispersions for bonding Cellophane, also employ glycerin. Of interest in this connection is the fact that alkyd resins also have been included in Cellophane adhesives.<sup>15</sup> These synthetic resins, usually made by the interaction of glycerin and phthalic anhydride, with suitable modifiers, have long been employed in making tough, durable protective coating. However, they are finding extensive employment in other phases of modern industry, including uses in bonding agents and sealing compounds. Examples of this last usage are to be found in can-sealing compositions.<sup>16, 17</sup> Glycerin itself is also employed as a plasticizer for compounds used for like purposes, a fact evident from the following formula taken from a British patent<sup>18</sup> covering sealing compositions for composite containers:

	Parts by Weight
Barytes .....	10.1
Asbestine .....	5.0
Gum Karaya .....	0.3
Colloidal Clay .....	1.9
Glue .....	4.5
Glycerin .....	2.5
Casein .....	1.8
Ammonia (28%) .....	0.7
Rubber Latex (Solids) .....	2.0
Vulcanized Rubber Latex (Solids) .....	5.0
Water .....	66.2

This brief review of glycerin in modern packaging adhesives gives only a few of its many uses in this industrial field. Many other examples could be cited to show the value of this versatile compound as a hygroscopic agent and plasticizer for these products and related items.

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## CHAPTER III

### CLEANERS AND POLISHES

THE IMPORTANCE of taking care of what we have has dictated increased use of cleaners and polishes for furniture, leather, and metals. It is good to know that glycerin, a major ingredient of many of these products, is available in almost limitless quantities to industry.

Glycerin is a clear, colorless, heavy, syrupy fluid that mixes freely with water and alcohol. An excellent solvent for many substances, in suitable concentration, it serves also as a valuable suspending agent for insoluble substances. This factor is of obvious value in many polishes where mild abrasives, such as may be used in furniture polishes or harder abrasives for metal polishes, must remain in suspension to be effective.

Another important characteristic is the hygroscopic action. It enters into the formulation of many types of cleansing and polishing agents where its several beneficial effects contribute considerably to the effectiveness of the products. Through its ability to attract and retain essential moisture, glycerin prevents the drying out of polishing pastes and helps to retain the effectiveness of polishing cloths by avoiding the "dusting out" of the dry ingredients. Authorities <sup>1, 2, 3, 4</sup> in the polish field frequently point out that glycerin is added to these products as a "wetting" agent, thus aiding in the removal of dirt and surface grime. A little glycerin also facilitates application.

This compound is especially useful in the emulsion types of furniture polish, now so popular. These combinations, through the aid of a suitable emulsifying agent, such as soap, gums or the like, combine the cleansing properties of water and water-soluble ingredients with the polish and gloss of oils.

Since the emulsifying agent plays an important part in the manufacture of this type of polish, specialists in the field often discuss these products on the basis of the emulsifier used. What-

ever the emulsifier used, however, glycerin is often included in the typical formulas. For example, where water-soluble gums are employed as the emulsifiers, a typical glycerin-containing furniture polish, given by Small,<sup>1</sup> may be prepared from:

	%
Kerosene .....	5.0
Light Mineral Oil .....	5.0
Glycerin .....	4.0
Gum Arabic .....	1.0
Gum Tragacanth .....	1.0
Water .....	84.0

Sometimes a combination of gum and special soap, such as triethanolamine oleate, is used in making emulsion furniture polishes, as in the following formula:<sup>2</sup>

	%
Mineral Oil (Sp. gr. 0.8769 at 60°F.) ...	11.0
Blown Castor Oil .....	1.0
Glycerin .....	5.0
Alcohol .....	5.0
Triethanolamine Oleate .....	1.0
Gum Tragacanth .....	0.5
Diatomaceous Earth .....	12.0
Water .....	64.5

During recent years, more specialized synthetic emulsifying agents have begun to be employed in making furniture polishes. As might be expected, these newer products are protected by patents. Here again, glycerine is specified, as in the following product,<sup>6</sup> utilizing the sodium salt of a fatty alcohol sulfate as the emulsifying agent and a water-soluble gum:

	%
Neutral Oil .....	17.00
Glycerin .....	5.65
Diatomaceous Earth .....	12.25
Amyl Acetate .....	0.25
Formaldehyde .....	1.00
Gum Tragacanth .....	0.20
Sodium Alkyl Sulfate .....	0.50
Water .....	63.15

The value of glycerin was appreciated many years ago as is evident in older types of polishes made without emulsifiers to disperse the water and oil phases. Such products, which require shaking before use, often contained special cleansing agents, such as antimony trichloride.

Here is an example of a product intermediate in type between the modern emulsion polishes and the much older straight oil furniture polishes: <sup>3</sup>

	%
Light Mineral Oil .....	58.0
Antimony Trichloride .....	2.0
Glycerin .....	7.0
Water .....	33.0

Older combinations, based on oils and solvents also occasionally used the characteristics inherent in glycerin; this despite the fact that glycerin is generally not miscible with many fixed oils and organic solvents. A liquid mixture for cleaning and polishing varnished wood surfaces, patented more than ten years ago, will serve to illustrate glycerin usage in such products: <sup>7</sup>

	Parts by Weight
Linseed Oil .....	3
Olive Oil .....	3
Oil of Rosemary .....	1
Glycerin .....	4
Oil of Cedar .....	2
Banana Oil .....	1
Spirits of Turpentine .....	12

Metal polishes may depend upon an abrasive action, a chemical action or, in some instances, on a combination of both effects. Glycerin is used in connection with these several types of products. One has come to realize that there is no such thing as a perfect universal metal cleaner. Polishes made for iron and steel, for example, are not suitable for aluminum or other softer metals. According to Tyler,<sup>4</sup> silver polishes may be suitable for pewter or gold, since they all belong more or less in the same class with regard to hardness, but they are totally unfit for polishing brass. Thus, metal polishes must be further subdivided on the basis of the metal to be cleaned.

Polishes for the harder metals often contain abrasives of varying degrees of fineness and hardness. Glycerin is frequently employed in the formulation of such items and it serves as a suspending, hygroscopic or wetting agent, depending upon the type of product. One mixture<sup>8</sup> suitable for polishing metallic articles is specified as containing glue, glycerin, borax, alundum and water. Expert metal workers often use simple suspensions of abrasives in glycerin for fine metal polishing work. Jewelers, for example, use ruby powder in glycerin-containing pastes, for polishing and buffing platinum and its alloys, rhodium and other hard precious metals.<sup>9</sup>

Metal polishing cloths containing mild abrasives enmeshed in the fabrics are made by dipping suitable materials into glycerin-containing preparations. Illustrative is the following procedure:<sup>5</sup>

	Parts by Weight
A. Hard Soap .....	5
Boiling Water .....	35
Glycerin .....	5
B. Oleic Acid .....	7
Pine Tripoli .....	35
C. Ammonia (0.96) .....	5
D. Alcohol .....	8

Solution A. is heated, B. added, and the whole saponified with C. Then the mixture is cooled to 40–45°C. and D. is poured in. Suitable cloths are impregnated at 40–45°C., permitted to dry, dusted out gently and packed.

The patent literature also offers examples of such glycerin-utilizing metal cleaning and polishing cloths. According to one British patent,<sup>10</sup> to make such a product, a lap of blended and shrunk cotton and wool fibers is impregnated with an aqueous solution containing:

	Parts by Weight
Magnesium Sulfate .....	60
Alum .....	35
Magnesium Chloride .....	5

It is then immersed in crude glycerin, pressed between polished and heated steel rollers smeared with tallow, allowed to dry and impregnated with a mixture of:



Olein .....	13.5 kg.
Ammonia Solution (Sp. gr. 0.88) ..	4.5 kg.
Silesian Chalk .....	31.75 kg.
White Spirit .....	40.0 l.

Metal cleaning compounds based on chemical action likewise utilize glycerin. Most such preparations, being based upon powerful chemical substances, are generally indicated for industrial rather than home use. Therefore, they should be used with full understanding of their possible dangers and due precautions taken. Thus, for cleaning off dirt, oil, colors, etc. from iron, steel and sheet metalware during and after manufacture, a European authority <sup>11</sup> recommends the use of a solution consisting of:

Soda Crystals .....	4 kg.
Sodium Hydroxide .....	250 g.
Glycerin .....	125 g.
Potassium Manganate .....	16 g.
Water .....	120 l.

Another liquid cleansing composition depending upon chemical action, specified as being suitable for use on metal or glass surfaces, can be made from the following ingredients: <sup>12</sup>

	%
Glycerin .....	0.125
Oxalic Acid .....	5.625
Potassium Chromate .....	0.25
Water .....	94.0

A patented formula for cleaning magnesium and magnesium base alloy surfaces <sup>13</sup> recommends an aqueous mixture such as the following:

	%
Water .....	70
Sulfuric Acid .....	5
Glycerin .....	25

Since glycerin enters extensively into glass cleaners and polishes, it is not surprising to find similar uses for it in preparations for treating polished metal surfaces. One such composition <sup>14</sup> consists of:

	Parts by Weight
Lard .....	10
Paraffin .....	4
Naphtha .....	1
Glycerin .....	1

Aluminum polishes are often somewhat specialized and take into consideration the properties peculiar to this widely used metal. Glycerin also takes its place in preparations for polishing aluminum, as is evident in the following formula: <sup>5</sup>

	Parts by Weight
Whiting .....	75
Pine, Yellow Tripoli .....	20
Sodium Bicarbonate .....	3
Potassium Sulfocyanide .....	2
Glycerin (25% Aqueous Solution)	

Sufficient to Make a Paste

It should be noted that the presence of a cyanide salt makes this a poisonous composition.

Tests have shown that a cleaning reagent comprising 33% of water, 56% of sodium bicarbonate, 10% of soft soap, small amounts of sodium carbonate and glycerin, and traces of iron and aluminum oxide has no harmful effects on aluminum.<sup>15</sup>

Silver polishes which are also useful for similar soft metals, such as pewter and gold, may contain glycerin as a wetting agent.<sup>4</sup> In 1936, a patent was granted in France for a silver polish consisting solely of a paste made from glycerin and sodium bicarbonate.<sup>16</sup> However, other glycerin-containing silver polishes are not quite so simple. An interesting example is given in a procedure for making silver polishing cloths: <sup>5</sup>

	Parts by Weight
A. Diglycol Stearate .....	15
Water .....	55
B. Glycerin .....	5
C. Precipitated Chalk .....	10
Magnesium Carbonate .....	10
Paris Red (Lead Oxide Red) .....	5

A. is heated until solution takes place, B. is poured in and finally C. is added through a strainer and with constant stirring. Rags or

cotton pads are impregnated with this mixture at 30–40°C. The excess liquid is pressed out between rollers and the polish is then dried.

A more specialized product for polishing gold, said to be patented,<sup>5</sup> is made from:

	Parts by Weight
Soap .....	20–25
Coconut Oil .....	1
Precipitated Chalk .....	25
Kieselguhr .....	8
Glycerin .....	40–45
Lemenone or Other Odorizer .....	1

Mention may be made of other metal cleaners not often discussed these days but which still command a respectable market. These are the old-fashioned stove polishes or, more properly, stove blackings. Many of these products contain glycerin. For example, a typical stove polish can be made as follows:<sup>6</sup>

	Parts by Weight
A. Graphite .....	24.0
Crude Glycerin .....	5.0
Formaldehyde .....	1.0
B. Hard Soap .....	3.2
Water .....	26.0
Paraffin .....	4.0

Solution B. is prepared by boiling and stirring, and added to the paste made by mixing A. The polish is stirred till cool and poured into suitable containers.

An older but simpler method for making a stove polish requires that graphite be mixed with waterglass to form a smooth paste. For each pound of paste there is added one ounce of glycerin and a small quantity of aniline black. Such a product is applied with a stiff brush.<sup>17</sup>

It can be seen that glycerin is a standard component of many wood and metal polishes and cleaners both old and new.

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## ELECTRICAL EQUIPMENT

IN THE production of many of the modern electrical appliances, glycerin is almost a vital material. Not only is glycerin widely employed in the manufacture of the electrolytic condensers, such as are used in radios and in the production of the colorful neon lights and other forms of discharge tubes, but it also finds an important place in the newer processes for electro-deposition and treatment of metals. Glycerine-containing resins, too, are coming in for a large share of electrical usefulness as insulating agents, binders and the like.

Although glycerin is a polyhydric alcohol, electrochemical studies have shown that, the addition of even large amounts of glycerin-water solutions to aqueous acetate or phosphate buffered solutions or to dilute hydrochloric acid or sulfuric acid solutions affects but slightly the hydrogen ion concentration as measured by means of a hydrogen electrode. However, in contrast to ethyl alcohol, one would have expected in glycerin solutions more ions, but actually there are so few that the electrode potential remains practically unchanged.<sup>1</sup>

The most important general use for glycerin is probably in the manufacture of electrolytes for electrolytic condensers. Literally scores of patents are available on this application alone during the last few years. As a rule, these electrolytes are simple combinations of glycerin with boric acid or sodium borate, and are used for making semi-dry electrolytic condensers. Typical examples of such glycerin usage are given by patents for making electrolytic condensers. In one patent,<sup>2</sup> electrode foils such as those of aluminum or tantalum with interposed spaces are assembled into a roll, and the roll is impregnated in an electrolyte, comprising as a major active ingredient a weak acid such as boric, phosphoric or citric acid and glycerin. Excess electrolyte is removed from the condenser by subjecting it to treatment with a

boric acid solution. In another process,<sup>3</sup> a mixture of boric acid, glycerin and ammonium hydroxide is heated to about 125°C. to form the electrolyte. The resulting supersaturated solution is added in vacuo to the previously exhausted condenser rolls. The vacuum is then destroyed and the solution is heated till a boiling point of 132°C. is reached. An illustrative film-forming electrolyte paste for electrolytic condensers is given in this patented formula:<sup>4</sup> 36% glycerin, 56% ammonium borate, 7% potato starch, and 1% agar-agar are mixed together. In another, similar combination, ammonium bicarbonate, ammonium carbonate and boric acid are used together with glycerin.<sup>5</sup>

Other modifications of the glycerin-containing electrolytes are also available in the patent literature. For example, a liquid and viscous electrolyte for an electrolytic condenser, which on cooling sets solid and "rock-hard," is formed from boric acid, glycerin and urea or aniline. This electrolyte, it is stated, may be used for impregnating a rolled material such as a cloth roll, and is also suitable for use as a casing or to have a casing molded directly around.<sup>6</sup> A polarizing electrolyte mixture suitable for dry-type, high-voltage electrochemical condensers, can be made by using together glycerin and gum arabic and a dispersed powdered oxide, such as aluminum oxide. This forms a substantially solid mass on setting.<sup>7</sup>

Glycerin is employed in other ways, too, than as an electrolyte in electrolytic condensers. As shown by a patent, the surface of the electrodes is increased by chemical corrosion, washed with hot and with cold water, and then with boiling glycerin and if desired, again with water. In this way, the products of the corrosion are completely removed.<sup>8</sup> Many other instances of the employment of glycerin in electrolytic condensers could be readily cited; but these serve to give some idea of the use of the compound in this connection.

The manufacture of gas-filled electric luminescent discharge tubes and the like offers another use for glycerin. In this connection, glycerin is particularly valuable as a binder for coating the interiors of the tubes with luminescent materials, although this application is by no means the only one. One patent,<sup>9</sup> which clearly and specifically indicates the role of glycerin in this process, is typical of most of these protected procedures. Here it is specified that in the manufacture of luminous electric discharge tubes

having an internal coating of luminescent materials, grease is removed from the envelope, before the coating is applied, by washing with alcohol and drying with ether. A sponge soaked in a binder made of glycerin 5 parts and boric acid 1 part is then passed to and fro through the tube. The amount of binder on the sponge is reduced at each passage and a dry sponge is finally passed through the tube in both directions, a thin invisible film of the binder being left on the envelope. A mixture of zinc sulfide and cadmium sulfide containing the usual impurities is then introduced as a fine powder and shaken to coat the tube evenly and to remove the excess of the powder. After this, the glycerin-containing binder is removed by heating and electrodes are sealed into the ends of the tube. The tube is evacuated and baked and gas is liberated from the electrodes by a high tension discharge. A rare gas (neon, argon, helium) is then introduced. If a metal, such as mercury, is added, the quantity is just sufficient to provide the vapor necessary during operation of the tube.

The method for applying the glycerin-boric acid binder in the above process is protected by a separate patent.<sup>10</sup> Other inventors have, however, used identical<sup>11</sup> or very similar<sup>12</sup> binders. In some patents, the employment of glycerin alone as a cementing agent is advocated in the manufacture of gaseous electric discharge for binding the luminescent materials.<sup>13, 14</sup> Here, too, other instances of the advantageous utilization of glycerin could readily be given.

The function of glycerin in these products is not, however, limited to its use as a binder. In one fairly recent patent,<sup>15</sup> free organic acids, such as oxalic, tartaric, benzoic or salicylic acids or their ammoniacal salts, are added to glycerin-containing solutions of one or more soluble compounds and alkaline earth metals. The salts formed are in the colloidal state and may be used for the manufacture of cathodes for electrical discharge tubes by precipitation on a support and heating to incandescence to form the oxides. Another method<sup>16</sup> for making oxide-coated cathodes for discharge tubes employs anhydrous glycerin which is mixed with an alkali earth metal compound such as the hydroxide. Carbon dioxide is then introduced into the mixture to disperse carbonate particles of the metal. This is then diluted with water to the desired consistency, a cathode to be coated is submerged in the solvent and a current is passed through the cathode and solvent to

cataphoretically deposit the particles on the cathode and to decompose the carbonate to form an oxide as a coating.

Graphite electrodes for discharge devices may also employ glycerin in their preparation. Such electrodes are freed from dust by heating to 1000°C. and quenching in a 25% glycerin solution. After quenching, the electrode is dried at 1200°C. or *in vacuo*.<sup>17</sup> Glycerin, according to one process,<sup>18</sup> also plays a minor role in the production of getters for fixing residual gases in evacuated housing, such as discharge devices.

An important place has been found for glycerin in the field of metal electrodeposition and treatment. For example, in electroplating iron with chromium, nickel, tin, lead, gold, silver, copper, bronze or cobalt, the iron object to be plated is dipped in a fused mixture of zinc 60%, tin 20% and lead 20%. The surface is amalgamated by dipping the object into a mercury salt solution containing glycerin and electroplating is then effected by the ordinary methods.<sup>19</sup> A nickel plating bath, that has been frequently recommended,<sup>20</sup> consists of:

Nickel Sulfate .....	4 oz.
Nickel Ammonium Sulfate .....	6 oz.
Boric Acid .....	2 oz.
Glycerin .....	1 oz.
Water .....	1 gal.

For cadmium plating,<sup>20</sup> this solution given below may be used:

Cadmium Hydroxide .....	48 g.
Sodium Sulfate .....	60 g.
Sodium Cyanide .....	120 g.
Glycerin .....	12 g.
Nickel Sulfate .....	1.5 g.
Water .....	1000 ml.

In electroplating, parts of articles not to be plated are stopped off with a film of a wax-like chlorinated naphthalene which is applied in the following way: the article is first painted over the areas to be plated with a resist consisting of a solution of a water-soluble adhesive, such as gum arabic, and a water-soluble plasticizer, such as glycerin. It is then dried and dipped into a melt of the chlorinated naphthalene and allowed to drain. The wax-like film breaks



away from the resist-coated parts, but adheres elsewhere. The resist is then removed by dissolving in warm water.<sup>21</sup>

Glycerin enters quite extensively in the electrical treatment of aluminum and its alloys. In one patent,<sup>22</sup> these metals are coated by anodic treatment in an alkali metal hydroxide solution to which glycerin is added. A suitable bath consists of 20 g. of 98% sodium hydroxide dissolved in one liter of water with the addition of either 150 ml. of glycerin or 125 ml. of glycerin and 20 ml. of 40% formaldehyde. Other additions are also recommended. The baths are operated at 10 to 15 volts with a current density of 18 to 24 amperes per square foot at 15–20°C. In another process for the electrolytic surface treatment of aluminum, an oxide layer is formed in this metal by anodic treatment in a non-aqueous bath which comprises a solution of boric acid or of an organic acid (citric, tartaric or lactic acid) in glycerin. The bath also contains a salt such as ammonium carbonate. The bath is maintained at 120–140° and the current density is such that the anode attains a temperature of about 200°C.<sup>23</sup> Other methods for the electrolytic treatment of aluminum and its alloys similarly use glycerin. Young,<sup>24, 25</sup> writing on the methods of coloring metals by electrochemical means, suggests the use of glycerin as an inhibitor for aluminum and its alloys. This prevents excessive etching and helps produce smooth, white surfaces.

The modern glycerin-containing synthetic resins, more generally known as glycerol-phthalate, alkyd or "glyptal" resins are also very widely employed in electrical materials. Their use is growing, since these resins can be readily modified for a large variety of purposes. The electric, chemical and physical properties of the alkyd resins have been extensively studied by Kienle and Race,<sup>26</sup> and reference to their work will be of interest to those planning to use these materials. Like glycerin itself, the resins compounded with this fluid are used as binders for luminescent materials associated with electric discharge devices.<sup>27</sup> Glyptal resins are also used for making molded, heatproof caps for such equipment.<sup>28</sup> Protective covers for electrical heating units may also be made from condensation products of glycerin and phthalic and succinic acids, according to one patent.<sup>29</sup> In making resistance elements, a conductive material, such as lampblack, is used with an alkyd

resin about 75% and about 25% of Chinese wood oil.<sup>30</sup> Metal laminations for electromagnet cores or other electrical apparatus are held together by glycerin-phthalic-anhydride resins according to foreign procedure.<sup>31</sup> An American process uses similar resinous compositions for coating wire.<sup>32</sup>

These patented processes aptly illustrate the adaptability of the glycerin-containing resins, but probably their greatest value is in the manufacture of insulators and insulating materials. The alkyd resins are used in rendering insulators permanently flexible, according to a French patent.<sup>33</sup> Starting with materials such as glycerin, phthalic anhydride, shellac and oleic acid, American inventors have prepared resinous compositions which are especially suitable for electric insulation.<sup>34</sup> Fibrous insulation, such as cotton, silk, asbestos, glass or paper, is bonded or united to a base or enameled conductor by means of a thin film of an alkyd resin made with or without the admixture of shellac according to the specifications of one process.<sup>35</sup> Other electrical insulating materials may combine other synthetic resins with the basic glycerin-containing synthetics.<sup>36</sup>

Glycerin enters into the production of a large number of miscellaneous electrical items. Glycerin is sometimes employed in electric batteries, usually as a constituent of the electrolyte. For instance, an electrolyte for charging batteries is made by mixing water with magnesium sulfate in the proportion of 10–95% by weight, adding zinc sulfate 2–8% and colloidion 2–10% as well as glycerin and aluminum sulfate. After twenty-four hours, sulfuric acid is added until a density of 1.225–1.280 is reached.<sup>37</sup> Another similar liquid, suitable for use as the formation liquid for lead electrode plates or for the electrolyte of the battery, consists of a mixture of magnesium sulfate, sodium sulfate, aluminum sulfate, ammonium sulfate, sodium potassium tartrate, glycerin, cochineal and aniline dissolved in water to which sulfuric acid is added.<sup>38</sup> In a special storage battery, in which the electrolyte is a solution of sodium hydroxide, glycerin is added to lessen the chemical action at the negative electrodes.<sup>39</sup>

Special electrodes are covered with microporous layers by first dipping them into a coagulating medium, such as a solution of sulfuric acid and glycerin and then into a mixture of latex with sulfur, washing with water and vulcanizing while wet.<sup>40</sup> Glycerin

is also employed as a flexibilizing agent in insulating electrical conductors, such as wires.<sup>41</sup> Enamels used for making electrical resistors sometimes use glycerin as a binding agent for the dry ingredients prior to baking at high temperatures.<sup>42</sup> An electrical conducting cement, with a variety of potential applications,<sup>43</sup> can be made by combining:

Lampblack .....	1
Litharge .....	2
Glycerin .....	3-8

The quantity of glycerin used varies with the final hardness and setting time desired.

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## CHAPTER V

# EXPLOSIVES

THE APPLICATION of glycerin as a component of explosives is probably its most generally recognized use. In this much publicized capacity, it is not as glycerin, but as the product of the reaction of glycerin and nitric acid, namely nitroglycerin (glyceryl-trinitrate) that it plays so extensive a part.

The history of nitroglycerin goes back nearly one hundred years (1846) to the work of Ascanio Sobrero in Italy who came upon it while testing the action of nitric acid on various organic substances. For two decades after this, it remained a laboratory curiosity. Nitroglycerin by itself is difficult to handle. Being a liquid it will leak from many types of containers, and then spread in a thin layer. Even this thin layer will detonate at the slightest blow, and consequently the early attempts to use it were frequently disastrous and its use was, therefore, discouraged.

It was not until 1862 that Alfred Nobel recognized the technical importance of nitroglycerin as an explosive, and first used it as a blasting agent. He was responsible for the building of the first plant for its production at Hilenborg, in Stockholm. This factory, which was the forerunner of his finally successful attempts to combine nitroglycerin in a form which would be safe to handle and at the same time retain its explosive characteristics, was destroyed by explosion after two years.

Shortly after that, the first German factory for the production of nitroglycerin was built at Krummel. This one proved more successful. During the first world war it was still in operation and producing from 45-50 thousand pounds of nitroglycerin per day.

It was in 1867 that Nobel discovered that kieselguhr was capable of absorbing three times its weight of nitroglycerin, which led to the eventual widespread use of it as an explosive. The plastic product which he obtained proved comparatively safe to handle.

Nobel called this product dynamite, and worked out modifications. In 1875, he invented blasting gelatin, a solution of nitroglycerin in nitrocellulose. The next step in 1886 was the development of ballistite, a powder obtained by gelatinizing a low-nitrated cotton with nitroglycerin. Shortly after this, a modification of ballistite known as cordite was adopted as a smokeless powder. This propellant consisted of a high nitrate gun cotton gelatinized by means of acetone, and into this mixture nitroglycerin and petrolatum were incorporated.

The history of nitroglycerin explosives from here on is merely the story of the improvements made upon this original work of Nobel and Sobrero.

Dynamite as it is manufactured today has many modifications. It has become largely an industrial explosive and approximately 300,000,000 pounds of it are consumed in a year of normal business in the United States, for mining, quarrying, engineering, harbor improvement, agricultural and other purposes.<sup>1</sup> The sensitive qualities of dynamite and its disruptive force make it unsuitable as a propellant in rifles or cannon, but it does have its place in military explosives, as will be pointed out later.

The majority of dynamites in the United States consist of an explosive compound, usually nitroglycerin, mixed with an absorbent composed of sodium nitrate and wood meal. The proportions are so chosen that the mixture will have an excess of available oxygen on explosion, and will, therefore, produce a minimum of poisonous gases. The use of the original absorbent, kieselguhr, has been completely abandoned, since it acted as an inert filler and thus reduced the strength of the dynamite. The materials which have replaced it, wood pulp or other fuel and the oxidizing salt, absorb the nitroglycerin and at the same time contribute to the heat and energy developed by the explosion.<sup>2</sup>

Dynamites over the years have extended to diversified mixtures, all having nitroglycerin as the base. Today a score or more of different dynamites are distinguished.<sup>3</sup> They all, however, have the common property of not exploding by simple inflammation, shock or moderate friction. They explode only by the use of strong caps, detonators, generally composed of mercury fulminate or some similar compound.

The straight nitroglycerin dynamites are made in strengths

from 15–60% and have a high rate of detonation and are, therefore, used only where quick action or shattering effect are desired. They resist water fairly well so that they may be used for under-water blasting, but are not as well adapted to this type of work as others which are designed specifically for this purpose. The best for this under-water work is gelatin dynamite which, instead of containing straight nitroglycerin, is a colloidal solution of nitroglycerin and nitrocotton. This is absorbed on a mixture of sodium nitrate and wood meal. The plastic consistency of the resulting product allows it to be extruded through a mold of the required diameter into paraffin paper cartridges. The strength of these dynamites ranges from 20 to 90% and they produce the least amount of noxious gases of any type of explosive.

Another of the variations of dynamite is ammonia gelatin dynamite. This resembles the gelatin dynamite except that a portion of the nitroglycerin-nitrocotton colloid is replaced by ammonium nitrate. The explosive characteristics are similar to those of gelatin dynamite.

One of the most widely used dynamites is blasting gelatin. This contains nitroglycerin which has been dissolved in nitrocotton to form a jelly, along with a small amount of antacid such as chalk. This explosive is tough and rubbery. Water has no effect upon it and it is used where the greatest possible concentration of energy is desired. Blasting gelatin is one of the quickest explosives manufactured for commercial use.

In recent years, the production of poisonous gases from dynamites has been reduced by improving the oxygen balance of the ingredients, thus making a great step forward in the safety measures attached to the use of this material. The actual employment of these dynamites and other explosives in the United States is somewhat regulated by the U. S. Bureau of Mines. Explosives to be used under given conditions are tested, and if they meet the specifications demanded by the U. S. Bureau of Mines they are listed as "permissible explosives,"<sup>4</sup> However, the approval does not constitute final control of explosives, since the U. S. Bureau of Mines has no power to prevent the use of other materials. The regulations on this are made by the individual states.<sup>5</sup>

Whereas the few types of dynamites mentioned here find their widest application in the industrial field, glycerin derivative explo-

sives also have an important part in the manufacture of the weapons of war. Whereas pyropowder is the commonest material used in military explosives, there are some types of weapons which require the use of propellents that have a greater potential than pyropowder, or, which for special reasons are commonly provided with powders having compositions different from pyropowder.<sup>6</sup>

One of the most important of these propellents are the so-called double base powders. This term has been applied to the powders which contain nitrocellulose and nitroglycerin as the principal constituents. The powders which are used by various military services usually contain from 60–80% of nitrocellulose and 20–40% of nitroglycerin. Certain commercial powders used in sporting ammunition are of similar composition. However, they find their widest application in such things as trench mortars where especially rapid burning is desired. They are used too in certain high velocity weapons where the high potential of the double base powders are valuable.

The other most widely used propellant which employs glycerin as a starting material is that known as cordite. It was after the Franco-Prussian war that the other developments in explosives began to challenge the use of gun powder as a propellant. About 1884 the French developed a propellant containing nitrocellulose, barium nitrate, potassium nitrate and soda. Another popular propellant of the period was ballistite, containing 40–50% of nitroglycerin.

Whereas various propellents were used by other countries, none of these entirely met the requirements of the British Government and a committee was appointed to investigate propellents. The work, largely carried out at Sir Frederick Abels' laboratories in Woolwich Arsenal by Dr. W. Kellner, resulted in the development of cordite. It was so named because it was produced in the form of cords and differed from ballistite in that nitrocellulose was incorporated with the nitroglycerin by means of acetone, and mineral jelly was added for the purpose of lubricating the gun barrel. In the final tests, it was found that the mineral jelly was consumed in the explosion and, therefore, failed to perform its action as a lubricant. But the jelly was found to be an important constituent of the propellant because it lowered the temperature of



the explosion, reducing the erosion of the barrel while increasing the volume of the gas given off, and thus maintaining the power of the propellant.<sup>7, 8</sup>

The manufacture of this explosive was commenced at the Royal Gunpowder Factory, Waltham Abbey, England, in 1889. The principal defects of this propellant was its tendency to erode the guns, particularly those of high caliber, and the fact that it had a limited life when stored at high temperatures. Following the African wars, the composition of cordite was modified to reduce the explosion temperature even more. This was accomplished by increasing the nitrocellulose.

Cordite is still used in large quantity as a propellant by the British although it has not maintained its favor with the other countries. However, all nations at the present time use as a propellant either gelatinized nitrocotton alone or else gelatinized nitrocotton mixed with varying quantities of nitroglycerin as the basis for their so-called smokeless powders.<sup>6</sup>

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## CHAPTER VI

# LEATHER

LIKE MANY of the processes whose origins go back to antiquity, the tanners and producers of leather used many empirical, secret methods and materials. Being astute men, these tanners took advantage of new substances as they were evolved. So when Scheele discovered glycerin, and other perfected inexpensive methods of producing this clear, syrupy, hygroscopic fluid, it became a material of the leather industry.

Many of these old processes, employing the unique properties of glycerin, are in use today. The modern tendency, however, is to seek protection by patent, so that when looking for new methods, one invariably turns to these sources of information. Then, too, knowledge acquired by research men, who may or may not be associated with industry, is reported in the literature. Examining these sources, it is not surprising to find that glycerin serves many useful purposes in almost every phase of leather manufacture.

Early in the treatment of leather, glycerin begins to play its role. Moore describes a method for preserving green hides and skins by impregnating them in a water-soluble salt of barium, such as barium chloride and glycerin.<sup>1</sup> Another method, for skins and hides, further along in the tanning process consists in treating them with a wax emulsion containing glycerin.<sup>2</sup> Returning to the raw materials, the Russians, for example, employ a glycerin-containing paste which is used to unhair hides.<sup>3</sup>

In a listing of materials used in tanning, glycerin is included as a matter of course.<sup>4</sup> A glycerin compound such as sodium glycerophosphate is employed in the preliminary treatment of hides and skins to facilitate uniform tanning.<sup>5</sup> A similar pre-tanning preparation consists of formaldehyde (40%) 46 parts, glycerin 8 parts, barium chloride 16 parts and 40 parts of water.<sup>6</sup>

In the actual tanning, a mixture containing water, alum, sodium chloride, wheat flour, and glycerin is advocated for thin leather, such as that used in gloves.<sup>7</sup> For heavier leathers, such as sole leather, it is recommended that the cleaned, limed skins be treated for 16 to 24 hours in a bath to which the following mixture is added for each one hundred quarts of water. The mixture consists of potassium chromate 260 g., boric acid 200 g., formic acid 180 g., and glycerin 50 g.<sup>8</sup> In another connection when it is desired to convert the insoluble mineral salts used in tanning into soluble compounds, glycerin is employed to dissolve out the complex metallic oxides so formed.<sup>9</sup>

In order to prevent the stiffening of tanned hides, the next step must, of course, be the incorporation of softening agents during the fat-liquoring or greasing process. This procedure not only makes the skin pliant but also increases the strength of the leather.

Here, too, glycerin has many applications. Grasser points out that glycerin, because of its hygroscopic nature, is often used in the finishing of chrome tanned leather in which it is required to retain a certain degree of humidity.<sup>10</sup> In this connection, an observation made by Kubelka is interesting. He points out that there are two types of water absorption which occur in hides. The first is capillary absorption in which the water can be displaced by glycerin. In the second class, the water is combined to form a gel. When this occurs, the water cannot be replaced by other liquids.<sup>11</sup> Kubelka's findings, therefore, explain in part the value of glycerin in leather softening.

A German method recommends that after special preparatory procedures, the hides should be tanned and washed in the usual manner. Fat liquoring, however, is affected with a liquid containing about half as much glycerin as fat.<sup>12</sup> Another grease for leather combines lecithin, milk and glycerin. Thus, evaporated skim milk is dissolved in glycerin and mixed with soybean lecithin to give a good greasing preparation.<sup>13</sup>

A Russian method of preparing a fat liquor for hides takes into account the chemical, rather than the physical properties of glycerin. A heated mixture of oleic acid and fish oils is autoclaved in combination with glycerin and naphthenic acid. The purpose here is to esterify the free acids present in the mixture.<sup>14</sup>

Leather, such as African sheepskin, suitable for glove stock can be rendered mellow and pliable by treating it with a lubricant such as lanolin and oleic acid, emulsified with glycerin.<sup>15</sup>

Sometimes it is desired to treat the leather prior to tanning. One way that is employed requires that the pretanned leather be stretched and softened for forty-five minutes in a 10% salt solution containing 2% glycerin. After thirty minutes, the usual tanning with chromium salts is applied.<sup>16</sup>

Sometimes after hides have been tanned, it is desired that different portions receive different types of finishes, according to the varying quality of the skin. In order to facilitate this, the hides may be cut up into selected parts, and these parts are individually finished as required. In order to enable storage, without causing undue drying and cracking, the hides may be conditioned after a chrome bath, by soaking them in a solution of sodium chloride, sodium sulfate, glucose and glycerin. Alum-tanned hides may be similarly treated. Later, as the need arises, the different portions may be fat-liquored and so on to the final finished product.<sup>17</sup>

Bennet describes a method for giving a white flesh side to calf leather.<sup>18</sup> Sumac-tanned skins are suitably prepared and treated with a special white dressing. After the skins have been thoroughly cleaned, they are coated repeatedly with a glycerin mixture. This mixture contains 100 parts of glycerin, 0.2 of salicylic acid, 0.2 of picric acid and 2.5 of borax. The skins are then nearly dried and, in a dark room, impregnated with a potassium bichromate solution. Drying is completed and the leather coated on both sides with a shellac varnish. Similarly, but not as the main ingredient, glycerin is part of the finish used when the sides are dyed blue or purple.

Glycerin plays a prominent role in finishing and dressing of all types of leather. In a comparative evaluation of the softening agents used in the preparation of casein-colored compositions for coating leathers, Russian investigators gave glycerin first place. In their studies, they found that the best results in plasticizing casein-pigment films on leather were obtained with the use of glycerin and a solution of soap in glycerin. They likewise found that the incorporation of glycerin in the pastes gives lasting, elastic pigment films.<sup>19</sup>

In view of the fact that it has been said that untreated casein

films possess little resistance to water, regardless of the kind of alkali used for dissolving the casein, and regardless of whether the leather surface is previously treated with ammonium hydroxide, acetic acid or alcohol,<sup>20</sup> the following water-stable glycerin-containing casein cover paint should be interesting. The casein dyes are dissolved in water and the solution brought to boiling. One kilogram of casein is dissolved in 5 or 6 liters of boiling water in the presence of 200 ml. of ammonium hydroxide until a paste is formed.

The glycerin and linseed oil are added. After emulsification, the solution is mixed with an aqueous emulsion of alizarin oil. Eight hundred grams of shellac are dissolved in 8 liters of boiling water in the presence of 160 cc. of ammonium hydroxide. After cooling, this last solution is mixed with the dye. These prepared solutions are then mixed to the desired density and dilute formalin added. The amount of glycerin added depends, apparently, upon the consistency of the mixture desired.<sup>21</sup> Keghel's formula for a gum lac casein finish for kid leather,<sup>22</sup> containing large quantities of glycerin is as follows:

A. Orange Shellac .....	3,000	g.
Caustic Potash .....	200	g.
Borax .....	900	g.
Ammonium Sulforicinoleate ....	800	g.
Nigrosine .....	500	g.
Formalin .....	100	g.
Water .....	14	l.
B. Casein .....	775	g.
Ammonia .....	400	ml.
Glycerin .....	1½	l.
Water .....	16	l.

The casein is dissolved in cold water and the ammonia and glycerin added, the mixture is well stirred and allowed to stand for 24 hours. The borax, caustic potash and the gum lac are dissolved separately. When thoroughly dissolved, the ricinoleate and the color are added. Finally the two solutions are mixed and the formalin is incorporated.

Several other glycerin-containing formulas (without casein), for various color shades, are given by Keghel. The following one, for brilliant black dressing, is typical:

Gum Lac .....	5	kg.
Solvay Soda .....	1	kg.
Caustic Potash .....	300	g.
Formalin .....	40	ml.
Ammonia .....	70	ml.
Glycerin .....	1.1	l.
Water Soluble Nigrosine .....	400	g.
Distilled Water .....	30	l.

The caustic potash and half the soda are added to boiling water. The gum lac is then added. The other ingredients are finally stirred in. After cooling, the formalin should be admixed.

A waterproofing coating for leather requires that the material is dipped into a bath or coated with the impermeabilizing agent. This preparation consists of a solution of a colloid, such as glue or gelatin, a plasticizer, glycerin, and an insolubilizing agent which usually is formaldehyde.<sup>23</sup>

The utilization of scrap leather has become an important part of the industry, since it offers economies of interest in reducing costs to both the consumer and the producer. Here glycerin continues to render excellent service. Ground leather is mixed with human hair that has been treated with a weak solution of sulfuric acid. The mixture is then impregnated with an emulsion of glycerin, oil, sulfur, and animal glue. The final product is suitable for sole leather.<sup>24</sup>

In the manufacture of waterproof products from animal fibrous material (e.g., leather), glycerin is employed to render the formed sheets waterproof, permanently soft and supple. This is attained by treatment with swelling agents and then with water-insoluble softening agents such as castor oil and the like. Tanning may be affected during, before or after softening and a water-resistant coating of a cellulose lacquer may be applied.

Untanned products are swollen with glycerin or a mixture of glycerin and methyl alcohol. After alternate swelling and pressing, the product may be further treated with glycerin or the alcoholic combination. Tanned products are softened by immersion in glycerin containing a little water, with or without the addition of alcohol. Tanning may be affected by using alum dissolved in glycerin.<sup>25</sup>

Films made from disintegrated fibrous materials from skins are

modified by adding glycerin and other substances, such as binders and wetting agents, before, during or after the disintegration. These final films which contain about 75% of water find use in prepared meat casings.<sup>26</sup>

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glycerin and an oxygenated pitch.<sup>5</sup> Lubricants comprising a hydrocarbon oil and a compound of furoic acid also contain small amounts of glycerin as an essential ingredient.<sup>6</sup> In a Russian method for making greases, naphthenic acids are heated with a small amount of lead oxide, agitated and heated to about 230°C. at a superatmospheric pressure together with fatty acids, glycerin and castor oil in the presence of iron.<sup>7</sup> These examples serve to illustrate the use of glycerin in petroleum lubricants, but numerous others could be as readily cited.

Glycerin also enters into the preparation of petroleum products in a variety of ways. In preparing lubricating and insulating oils used at high temperatures, glycerin may be used for purifying crude or sludged oil.<sup>8</sup> It may also be used in processes for extracting hydrocarbons which are further treated to make refined lubricating oils.<sup>9</sup> Glycerin-containing preparations are sometimes employed in desalting and demulsifying crude mineral oils. A formula of this type consists of approximately:

	%
Sodium Hydroxide .....	25
Sodium Acetate .....	10
Alcohol .....	20
Glycerin .....	10
Water .....	35-45

The oils are mixed in the continuous phase with this preparation.<sup>10</sup> Glycerin derivatives, such as glycerol tristearate are occasionally employed in dewaxing hydrocarbon oils.<sup>11</sup>

But glycerin has a very important place of its own in the lubricant field, and it finds major uses where petroleum lubricants could not be used. Because of its insolubility in most of the common organic solvents, glycerin finds many uses as a lubricant where these fluids are employed. Typical is this simple, easily prepared machine oil: <sup>12</sup>

	Parts by Weight
Oleic Acid .....	100
Glycerin .....	50

A grease insoluble in gasoline used for gasoline pumps and the like consists of: <sup>13</sup>



	Parts by Weight
Oleic Acid .....	2.5
Ammonium Linoleate .....	17.5
Glycerin .....	37
Lubricating Oil .....	35

Another compound, used for similar purposes, contains blown castor oil, glycerin, carnauba wax, and graphite.<sup>14</sup> In a more-recent foreign patent polyglycerins or compounds containing them are recommended as lubricants for machine parts which come into contact with solvents for fatty oils, fats and mineral oils.<sup>15</sup>

At the University of Michigan, Meloche and Frederick<sup>16</sup> developed an improved lubricant insoluble in organic solvents. They were interested in the use of such a product for laboratory work, but this lubricant is readily applicable in other fields. To make this glycerin-containing agent, the ingredients are mixed together to form a thick paste:

	Parts by Weight
Glycerin (Anhydrous) .....	25
Dextrin .....	7
d-Mannitol (c.p.) .....	3.5

These are heated carefully with stirring, until the solid material is dissolved and the solution just begins to boil. To increase the viscosity, more dextrin is added; to increase the fluidity, more glycerin is mixed in; to increase the greasiness, more mannitol is added.

These workers give a long comprehensive list of solvents which do not affect this lubricant and another list of solvents which but slightly affect it. However, in general, water, alcohols, aliphatic acids and certain amines and nitrogen-containing heterocyclic compounds prevent the use of this glycerin-containing lubricant. Another laboratory lubricant insoluble in the ordinary fat solvents, such as the hydrocarbons or chlorinated hydrocarbons, can be made by mixing glycerin and bentonite. The viscosity of the paste can be adjusted to suit particular needs, and even in the presence of water holds up remarkably well. Its viscosity does not diminish very much with rise in temperatures, even well over 100°C.<sup>17</sup>

Because of its low freezing point, glycerin-containing lubricants can be employed under extremely low temperature condi-

tions. Glycerin was used as a lubricant in the early days of electrical refrigeration and still finds such uses. Mixed with graphite, glycerin makes an excellent low temperature lubricant. In an extreme pressure lubricant in which dispersed candelilla wax is the major ingredient, up to 50% of glycerin is added as an anti-freeze agent.<sup>18</sup>

Of course, glycerin finds many uses in lubricants for special purposes. Glycerin, for example, is a standard ingredient of lubricants for rubber surfaces. Oil and greases cannot be used on the rubber shackles of automobiles and the like because of their deteriorating effects on this material. For lubricating these parts, a simple mixture of two parts of alcohol and one part of glycerin is highly recommended. The alcohol evaporates off, leaving a thin film of glycerin to perform its antifriction action. In addition to its function as a lubricant in rubber surfaces of all types of products, tubings, sheetings, blocks, etc., glycerin has a beneficial effect upon the rubber, maintaining it in its firm resilient condition and preventing drying and cracking. A patented lubricant for rubber bearings such as automobile spring shackles consists of a 50% aqueous glycerin solution used in admixture with about 0.2% of finely divided graphite.<sup>19</sup>

Glycerin is particularly important in the manufacture of explosionproof lubricants. These are used as lubricants where explosions are likely to take place due to high temperature and pressure with the usual lubricants. In one process, glycerin is polymerized by heating in the presence of copper chloride at 250°C. in a current of inert gas. If the product is too viscous, water is added, and gum tragacanth, talc or the like may be mixed in to give body to the lubricant.<sup>20</sup> The same inventor has prepared similar glycerin products for use as lubricants for apparatus and equipment coming into contact with compressed oxygen.<sup>21</sup> A group of authorities,<sup>22</sup> studying graphite alone, graphite mixed with glycerin, and tricresyl phosphate—talc mixtures found that none of these met the requirements for an explosionproof lubricant. Glycerin, they found, was the safest material to use.

Other processes are available for making important glycerin-containing lubricants for many purposes. In a Japanese process, glycerin, previously well agitated with an inert gas, such as carbon dioxide or nitrogen under pressure, is introduced into castor oil

which has been gradually heated to 200°C., causing polymerization of the oil and the combination of the two compounds to form a lubricant.<sup>23</sup> A non-greasy lubricant<sup>24</sup> can be made from:

	Parts by Weight
Sodium Alginate .....	19
Water .....	100
Glycerin .....	76

The ingredients are mixed to a smooth paste while heating to 100°C. and the glycerin is added. Then nearly all of the water is boiled off.

A lubricant suitable for use on pipe threads can be made, according to one patent,<sup>25</sup> by combining:

	Parts by Weight
Lime Tallow Soap .....	10.7
Mineral Oil .....	63.7
Glycerin .....	1.0
Water .....	0.6
Zinc Dust .....	20.0
Sulfurized Sperm Oil .....	4.0

A cold drawing metal lubricant containing a much higher proportion of glycerin is one made with:

	Parts by Weight
Dipotassium Hydrogen Phosphate .....	20
Water .....	80
Sulfonated Castor Oil .....	1
Glycerin .....	33

This material, used as a coating for metals, such as iron or steel, not only facilitates their working but also aids in subsequent painting or the like.<sup>26</sup> A molding press lubricant<sup>27</sup> can be made from such simple materials as:

	Parts by Weight
Salt .....	2
Water .....	7
Alcohol .....	1
Glycerin .....	1

Here again these examples merely serve to show the versatility and applicability of glycerin in all types of lubricants. Other

instances of such uses could be readily presented, space permitting.

Within the last few years, the glycerin-containing synthetic resins also known as alkyd, glyptal, glycerol-phthalate resins, have begun to find important uses in lubricant compounds. In one patented process,<sup>28</sup> which aptly describes the part played by these synthetics, the viscosity and oiliness of a lubricant are improved by colloiddally dispersing or dissolving in the oil a resinous product prepared by condensing 3 mols of polymerized oleic acid with about 2 mols of glycerin. The condensation takes place in an atmosphere of nitrogen heated to about 200°C. until the cooled mixture appears as a rubbery mass. It undergoes further treatment to meet the specified requisites of molecular weight and oxygen content. It has been found that 6% of this glycerin-containing resin, dissolved in lubricating oil, raised the oil's viscosity index from 25 to 114. Dibutyl phthalate properly thickened with 10% of glycerol phthalate resin (among other recommended additions) can be used as a lubricant capable of withstanding high temperatures without carbonization and possessing good lubricating and viscosity characteristics, according to a report made last year.<sup>29</sup> It should also be mentioned that glycerin is used as a lubricant for the synthetic resin bearings now beginning to find wide employment.<sup>30</sup>

Other glycerin derivatives find useful employment in lubricating preparations. Some of these, like the polyglycerols, and the resins, have already been mentioned. A synthetic glycerin ester, such as glycerol oleate, is recommended as an addition to viscous hydrocarbons used as lubricants for motors, particularly during the "running in" period.<sup>31</sup> In lubricants for fine instruments, such as clocks or the like, use is made of synthetically prepared esters of glycerin with fatty acids containing 5 to 12 carbon atoms.<sup>32</sup>

The examples given in this review are only a few of the numerous uses of glycerin in the lubricants field.

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## CHAPTER VIII

### METALS

IN METAL treatment and fabrication, glycerin has long had many uses. However, recent years have brought new applications for this versatile compound, and the literature, both technical and industrial, reflects the growing use in such diverse fields as electrolysis, metal quenching and tempering, molds, soldering fluids and fluxes, metal cleaning and polishing, special lubricants and metallurgical-analytic processes.

Glycerin is a well known agent in electroplating and stripping processes, and more recently, it is finding wide use in electrolytic polishing procedures and in the anodic treatment of aluminum. Standard glycerin-containing solutions, such as those for the electrodeposition of nickel and cadmium, have long been in use.<sup>1</sup> Mathers and Guest<sup>2</sup> have shown that glycerin increases the throwing power of zinc sulfate baths within a wide range of current densities. Moreover, they found that the zinc deposits seemed to be improved in quality.

An interesting example of the use of glycerin is given in a recent foreign patent<sup>3</sup> covering a procedure for the electrodeposition of tungsten alloys. According to the patent, lustrous tungsten-iron alloys are obtainable by electrolyzing a solution such as the following:

Sodium Tungstate .....	400 g.
Sodium Pyrophosphate (Dibasic) .....	400 g.
Potassium Chloride .....	100 g.
Ammonium Fluoride .....	40 g.
Potassium Ferrocyanide .....	2 g.
Potassium Hydroxide .....	100 g.
Water .....	600 ml.
Ethyl Alcohol .....	80 ml.
Glycerin .....	80 ml.

Electrolysis is preferably effected at 80°C., at a current density

of 0.12 amperes per square centimeter. After deposition on a metal, the alloy may be heated to 1000–1200°C., or more, to cause it to diffuse into the surface.

Metal stripping, the reverse of electrodeposition, likewise utilizes glycerin in standard formulas. A case in point is the following solution, used for stripping nickel from steel:

Sulfuric Acid .....	2 gal.
Glycerin .....	2 oz.
Water .....	1 qt.

This solution is used at room temperature, with a reverse current of six volts, employing lead cathodes. The rate of stripping may be increased by adding more water, but this addition will increase the tendency to pit.<sup>4</sup>

Precious metals may similarly be stripped one from the other by the use of glycerin-containing solutions. Thus, Kushner<sup>5</sup> suggests the following solution for stripping gold from silver:

Hydrochloric Acid (Concentrated) ..	4 oz.
Glycerin .....	1 fl. oz.
Water .....	1 gal.

The solution is employed cold, at six volts, with carbon cathodes. Agitation should be avoided since this tends to remove the thin protective film of silver chloride that forms on the base metal.

Electrolytic processes for polishing steel have found advantageous application for glycerin. Most significant in this connection is the work of Uhlig,<sup>6</sup> who reported that, by the use of a glycerin-phosphoric acid mixture, electrolytic polishing of 18/8 stainless steel is less expensive and less time-consuming than by mechanical procedure. The optimum polish was obtained by an electrolyte consisting of:

	%
Phosphoric Acid .....	42
Glycerin .....	47
Water .....	11

at 100°C. or more and 0.1 ampere per square inch. In this process, one function of glycerin is to prevent the pickling action of acid anodic solution. Other steels could be polished in the same

electrolyte, but the operating conditions would have to be somewhat modified. It has been found also that nickel, copper, chrome steel, and mild steel can be polished in this way.<sup>7</sup>

Glycerin has an established place in processes for anodizing aluminum in which corrosion-resistant oxide coatings, that can readily be colored with appropriate dyes or other means, are formed. Of the several procedures employed, the sulfuric acid bath, containing an inhibitor such as glycerin, is undoubtedly the most popular, since it gives a white, transparent, hard oxide coating which is an integral part of the metal.<sup>8</sup> In the role of an inhibiting agent, glycerin serves to prevent excessive etching and helps to produce a smooth white surface. It is employed as the retarder or inhibitor in several standard processes, including the Alumilite, Tennent's and Anotint procedures, all of which use sulfuric acid.<sup>9</sup>

From the patent literature, however, it is evident that the use of glycerin is not limited to methods employing only sulfuric acid. It is used also in anodic coating methods for aluminum which employ caustic soda<sup>10</sup> or chromic acid<sup>11</sup> or oxalic acid<sup>12</sup> in conjunction with other substances.

Since glycerin effectively bridges the gap between oil and water, it has long been advocated and frequently employed as a quenching medium for tempering steel.<sup>13, 14</sup> Much of the earlier data has quite recently been substantiated and elaborated by the comprehensive report of Richards.<sup>15</sup> Here the use of mixtures of glycerin and water was advocated as quenching agents for the tempering of steel in the region between oil-quenching and water-quenching. It was found that the higher the ratio of glycerin to water, the milder becomes the quenching. Considerable importance is attached to the fact that no dirt or deposits are formed on the metal. Moreover, traces of glycerin can easily be washed off. To produce high elasticity and maximum hardness, it is advised that glycerin should be the major constituent. However, elasticity may be enhanced by the addition of 0.25 to 4.0% of potassium sulfate or of manganese sulfate or, still more, by the addition of 1 to 2% of potassium chloride or 1 to 3% of manganese chloride. It has been observed that acrolein is not formed by the thermal decomposition of glycerin, if water is present.

However, according to Shoemaker's patent,<sup>16</sup> glycerin may be



employed in processes for protecting metals after the pickling process. In order to neutralize the adhering acid and to protect the surface from rusting, this patent specifies the rinsing of the metal after pickling, in solutions containing caustic alkali, glycerin, and a wetting agent, such as sodium metaphosphate or sodium hexametaphosphate.

Other processes for treating and cleaning metal surfaces likewise employ glycerin. Thus, according to a comprehensive European report,<sup>17</sup> a cheap solution for removing rust and forge scale from iron, steel, and sheet metal consists of:

Sodium Hydroxide .....	750 g.
Soda Crystals .....	875 g.
Potassium Permanganate or Potassium Manganate .....	10 g.
Water .....	12 l.

For cleaning of dirt, oil, colors, and like stains, a little glycerin is added without affecting the derusting action. After a few minutes in the solution, the rust dissolves and can be wiped off, the metal underneath remaining uncorroded and possessing a thin coating which protects it from rust for a short time.

When cleaning alone is desired, the following solution is recommended:

Soda Crystals .....	4 kg.
Sodium Hydroxide .....	250 g.
Glycerin .....	125 g.
Potassium Manganate .....	16 g.
Water (Hot) .....	120 l.

Mason<sup>18</sup> has described also an interesting composition for removing rust from metals, consisting of:

	Parts by Weight
Oxalic Acid .....	20
Phosphoric Acid .....	20
Glycerin .....	10
Ground Silica .....	50

This paste is placed on the ordinarily inaccessible surfaces and, after allowing it to stand in a warm place for 15–20 minutes, can then be washed off.

Glycerin, however, is not limited to use on cleaning ferrous metals. One patent,<sup>19</sup> for example, specifies the use of the following solution for cleaning magnesium and magnesium-base alloy surfaces:

	Parts by Weight
Water .....	70
Sulfuric Acid .....	5
Glycerin .....	25

Glycerin is a frequent constituent of standard polishing compositions for various metals.<sup>20, 21</sup> Of interest in this connection is Pyler's<sup>22</sup> suggestion that when heavy accumulations are encountered on stainless steel, iron-free emery of fine grit, with glycerin as a lubricant, will give excellent cleansing results.

Recent work indicates that glycerin may have a role in the molds used in making shaped metallic items. When particularly fine detail is desired for making small castings, Blann and Moore<sup>23, 24</sup> advocate the use of a mixture of FFF pumice-stone powder and glycerin in the proportions of 8:1. This is used in place of the foundry sand ordinarily employed. In this connection Dunbeck<sup>25</sup> reported that glycerin gives good results in preventing the too rapid drying of synthetic sands utilized for making molds.

Soldering fluids and pastes are compositions that frequently utilize the properties of glycerin, particularly its ability to "wet" metal surfaces. Many glycerin-containing soldering fluids are available and easily prepared, but the following, with a wide range of usefulness, is quite typical:

	%
Zinc Chloride .....	15
Glycerin .....	25
Water .....	60

This combination is said<sup>26</sup> to be satisfactory for use on copper, brass, steel, terne plate, tinned steel, monel, and others.

The following soldering fluid is interesting in that no metallic salts are used in its formulation:<sup>1</sup>

	Parts by Weight
Lactic Acid .....	1
Glycerin .....	1
Water .....	0

According to Watkins,<sup>27</sup> soldering pastes facilitate soldering by combining the solder with the flux in one preparation. Such products generally consist of powdered tin or solder or solder mixed with zinc chloride and ammonium chloride, glycerin, and water. Watkins states that the proportion of flux varies between 10 and 50%. Two glycerin-containing soldering preparations are included among the typical analyses of five such products given by this writer.

Gonser and Slowter<sup>28</sup> point out that some patented rosin-base fluxes attempt to combine the speed of an active acid flux with the protective action afforded by a rosin residue. As an example, they describe a rosin flux containing 1.5% of aniline hydrochloride and 1.5% of a solvent, such as glycerin. This composition is said to release sufficient hydrochloric acid by decomposition to speed the fluxing action, and yet to be comparatively non-corrosive.

Somewhat along these lines are the specifications given in a British patent<sup>29</sup> which claims that soldering fluxes may be prepared by mixing phosphoric acid with a mixture of powdered ammonium chloride, a liquid or pasty medium, such as glycerin, and a mass consisting wholly or mainly of rosin.

Glycerin also plays an important part in galvanizing or hot-dip tinning processes.<sup>30</sup> In 1931, Imhoff<sup>31</sup> explained the function of glycerin in such procedures as follows: "From a practical standpoint, at least so far as the galvanizer is concerned, the important features in the chemistry of using glycerin as a flux conditioner are that the glycerin provides a medium for supplying and holding water in the flux. Water is absolutely essential as the medium through which the flux can act and also through which the chemical reactions can go on. It also provides the fluidity necessary in a good working flux so that it can slip off the work easily and not burn on to it, as a dry cakey flux usually does." This authority also pointed out that a glycerin flux is thick and more or less viscous. It is much heavier than fluxes made up with other conditioners and is, therefore, considered excellent for use for heavier work.

In a discussion of the hot-tinning of fabricated articles, Daniels<sup>32</sup> notes that the usual zinc chloride or zinc chloride-ammonium chloride solutions used for fluxing copper wire, prior

to tinning, are being replaced by tin (stannous) chloride and glycerin or lactic acid and/or glycerin.

Glycerin is a frequent ingredient of the etching solutions that find such wide use in metallurgical microscopic analyses. Thus, for etching aluminum and its alloys, Egeberg and Promsel<sup>33</sup> recommend that the freshly polished, cleaned specimens are warmed in hot water and treated immediately with the following etching solution:

	Parts by Volume
Nitric Acid .....	1
Hydrofluoric Acid .....	2
Glycerin .....	3

This is similar to the etching agent suggested by Romig and Rowland<sup>34</sup> to reveal the iron-tin alloy layer on commercial hot-dipped tin plate; consisting of:

Nitric Acid .....	1 drop
Hydrofluoric Acid .....	2 drops
Glycerin .....	25 ml.

The ingredients are mixed well.

For white metals, such as tin, lead, antimony, bismuth and their alloys as well as Britannia metal, Egeberg and Promsel state that these metals are etched with the following solution:

	Parts by Volume
Nitric Acid .....	1
Acetic Acid .....	3
Glycerin .....	15

Aqua regia in glycerin is a standard etching agent for the microscopic study of stainless steels.<sup>35</sup>

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## PACKAGING MATERIALS

IN THE packaging industry and in the formulation of related products, several qualities of glycerin are being made use of. Of these properties, perhaps none is more important than that of being able to plasticize or flexibilize paper, cellulosic materials and the like. In paper products, for example, this plasticizing action may be attributed to a combined softening and lubricating effect. Part of this effect may be traced to the fact that as a first class hygroscopic agent, glycerin is able to attract and retain the moisture so essential to prevent excessive dryness with subsequent brittleness and cracking. However, one cannot overlook the fact, as pointed out by Connor and Nadelman,<sup>1</sup> that glycerin is an excellent softener for paper even at low relative humidity.

The high boiling point of glycerin assures its continued action at high temperatures. Thus, glycerin-containing packaging materials can be sent to even tropical or arid countries with a confidence that the wrappings will do a good protecting job. Conversely, the low freezing point of glycerin assures flexibility of the materials in cold or freezing climates. Indeed, this property forms the basis for its use in products for frozen foods.<sup>2</sup>

Paper and paper products are basic to the packaging industry. Glycerin has numerous uses in conjunction with paper products and their treatment, a fact clearly evident in studies of the industrial and technical literature reviewed elsewhere in this volume, and is considered one of the basic non-fibrous chemical raw materials of the paper industry. This chapter reviews briefly new developments in the paper industry which are especially pertinent to the packaging field.

As new types of paper finishes are developed or old ones improved, it will generally be found that glycerin has helped quite considerably in the achievement of these improvements. Thus

glycerin is a regular plasticizing constituent, not only of standard wrappings, but also of such specialties as glassine papers,<sup>3</sup> waxed papers, parchment papers, parchment-like papers, papers prepared especially for use in conjunction with foods<sup>4</sup> and many other types. The creation of such characteristics as greaseproofness, water repellency, and flameproofness in paper products likewise utilizes the several characteristics inherent in glycerin.

Today there is growing attention in the packaging field to wet strength in papers. In a recent and extensive review on this characteristic, Collins<sup>5</sup> pointed out that since there is a tendency for some wet strengthening agents or treatments to make the paper stiff, harsh or brittle, plasticizing or softening the sheet is of primary importance. His review of standard and patented methods for achieving this action clearly illustrates the wide use of glycerin in this connection. Thus, glycerin is used for softening viscose-treated papers, for plasticizing glue-treated sheets, for the plasticizing of urea-formaldehyde resin-treated sheets, and for the treatment of papers prepared with certain cellulosic derivatives. The patent literature offers additional instances in which this compound is used in the preparation of papers of high wet and dry strength.<sup>6</sup>

As previously indicated, glycerin enters extensively into special finishes or special treatments to render paper water, grease or fire-resistant. It likewise enters into other special coatings or proofings.<sup>7, 8</sup> In waterproofing, according to one patented example,<sup>9</sup> both glycerin and a drying oil are used together with a protein material, pigments, etc., to form paper-coating compositions. It is claimed that the conjunct use of the drying oil and glycerin gives especially good water resistance.

Glycerin comes into very extensive use in papers greaseproofing procedures not only as a hygroscopic plasticizing agent, but also to some extent as a barrier material to the fatty or oily materials. Thus, glycerin may be used with such greaseproofing materials as sodium silicate<sup>10, 11</sup> formaldehyde-treated glue or gelatin,<sup>12, 13</sup> zein (a corn protein),<sup>12</sup> cellulose derivatives,<sup>14</sup> and starches. One widely used preparation, a product that may be applied by brushing, spraying or dipping to provide a film on paper or fiber containers that is resistant to oils and greases, is made from:<sup>15</sup>

	Parts by Weight
Starch .....	6.6
Caustic Soda .....	0.1
Glycerin .....	2.0
Sugar .....	0.6
Sodium Salicylate .....	0.2
Water .....	90.5

Glycerin derivatives also serve useful functions in grease and oil-resistant treatments. Thus in one process,<sup>16</sup> polyglycerin is used to make coated paper bags suitable for holding oil for an extended time. In this instance, the glycerin derivative serves as a relatively non-volatile, oil resistant softener which prevents the paper from cracking or creasing during manufacture or use.

Of course, combined water and grease resistance can also be attained by the use of glycerin-utilizing compositions.<sup>17</sup> This versatile compound also extends its action not only to papers which are flame-resistant,<sup>18</sup> but also to paper-treating compositions which impart this characteristic and also resistance to grease and moisture.<sup>19</sup> In this latter instance, paper is impregnated under pressure with an aqueous solution of borax, sodium phosphate, ammonium phosphate, ammonium sulfate, gelatin and glycerin. The treated paper is dried and further impregnated under pressure with a solution of latex, partially dried and then treated to vulcanize the latex.

Obviously, the characteristics that make glycerin so valuable in paper sheets and the like also extend to heavier paper products such as cartons and containers made from paper board or paper fiber. Indeed, glycerin enters into the adhesives used in making the laminated containers of paper or the like.<sup>20</sup> Of course, many of the special finishes applicable to other paper products are useful in these products as well. However, the moisture and grease-proofing compositions may require slight modifications to meet the specific requirements of multiple boxes or laminated fibrous containers.<sup>21, 22</sup>

Sealing compositions for combination metal and fiber containers sometimes employ glycerin as a useful constituent. Illustrative is the employment of such a glycerin-containing highly viscous composition for securing metal ends to food containers



comprising a body made from one or more layers of fibrous material.<sup>23</sup>

No discussion of modern advances in paper treating compositions or packaging materials can be considered complete without mention of the glycerin-utilizing alkyd-type resins. These modern synthetic resins, based upon the interaction of glycerin with polybasic acids, such as phthalic acid, are modifiable to meet an almost infinite variety of needs. Noted for their beauty, resistance, durability and general toughness, these synthetic resins have a strongly entrenched position in the production of paints, varnishes, lacquers and other protective coatings. However, far from being limited to such uses, these modern synthetics are finding increasing use in other industrial fields as well. In the paper industry, these glycerin-utilizing resins have found employment for many diverse purposes, among them being coating, impregnating, laminating, and strengthening agents for paper and fiber products.<sup>2</sup> Other uses of recent origin include sizing compounds,<sup>24</sup> waterproofing compounds,<sup>25</sup> greaseproof coatings,<sup>26</sup> thermoplastic coatings,<sup>27</sup> resins emulsions,<sup>28</sup> and extenders for latex and rubber dispersions<sup>29</sup> for use in paper treatments.

Undoubtedly the greatest advance in modern packaging was the development and exploitation of regenerated cellulose products, generally referred to under the generic name of Cellophane. Glycerin is used in their production.<sup>30</sup> Thus during the 1940-41 period, about 14.2% of all glycerin consumed in the United States went into the manufacture of Cellophane. In 1944 and 1945, about 45% of the Cellophane produced was made with glycerin.<sup>31</sup>

One of the outstanding uses of glycerin in modern technology is its employment as a plasticizer for Cellophane. In the processing of these regenerated cellulosic transparent materials, bathing in a solution of glycerin and water is one of the final and most important steps. The glycerin which remains in the Cellophane to the extent of about 25% of the weight of the finished product imparts the necessary pliability to this widely used material. Without such a softening agent, the film is brittle and useless.

No one in the packaging industry need be reminded of the versatility of Cellophane as a packaging material. Newer work has only served to extend its fields of usefulness. During recent

years, glycerin-plasticized Cellophane has found increasing applications as a packaging material for frozen foods.<sup>32, 33</sup> Here its ability to remain fluid at low temperatures becomes a most valuable asset.

Years ago, it was recognized that glycerin and glycerin-containing compositions are hardly at all permeable to mustard gas. This characteristic of glycerin led to the study of cellulose preparations, especially Cellophane, and it was found that such compounds could be used for the protection not only of foodstuffs and clothes, but also the skin of human beings against mustard gas.<sup>34</sup>

In 1942, in a symposium on ways to decrease occupational dermatitis in war industries, Schwartz<sup>35</sup> of the U. S. Public Health Service pointed out that Cellophane, plasticized with glycerin, could be used to make protective clothes for workers. Moreover, Cellophane is not affected by acids or petroleum solvents and is also a good protection against certain toxic gases. However, he remarked that the disadvantages of Cellophane of being made brittle by water and of being inflammable could be overcome by suitable treatment during manufacture. Thus treatment with ammonium sulfamate could make the film fireproof, whereas coating it with a resin would make it waterproof.

According to one patent,<sup>36</sup> a transparent, flexible and pliable sheet, that is proof against water, organic solvents, and mineral and vegetable oils, is made from a cellulose hydrate material having a water and glycerin content combined with a special resinous coating.

In another patent,<sup>37</sup> a procedure is described for preparing a non-sticking, smooth, flameproof, transparent regenerated cellulose sheet material suitable for use as a wrapping material. According to the method given, gel-regenerated cellulose in sheet form is passed through an aqueous bath containing glycerin, ammonium sulfamate and an emulsion comprising carnauba wax, stearic acid, morpholine, shellac, monosulfonated alkyl benzene and water. After treatment in this solution, the film is dried.

Alkyd resins are also used in the treatments of these cellulose materials. In two recent instances,<sup>38, 39</sup> the resins are included in compositions for waterproofing these strips and sheets.

Glycerin is a frequent constituent of adhesives for Cellophane.<sup>31</sup>

Glycerin is a standard component of the materials used for producing, shaping, and treating cellulose bands, caps, seals, pellicles and similar items used to protect and decorate bottle closures, jar caps and other glass, ceramic or plastic packages.<sup>40, 41</sup> Glycerin not only serves to plasticize these materials, but is also a constituent of the preservative solutions in which they are stored prior to use.<sup>42</sup> The residual glycerin left in the bands and caps after they are applied and allowed to shrink on snugly prevents cracking and embrittlement.

Another application for glycerin in packaging materials was reported at a symposium on the preservation of foodstuffs under war conditions. At this conference, Katz<sup>43</sup> reported that the combination of gelatin and glycerin is very resistant to war gases. Treatment with formaldehyde or chromates is needed to make the gelatin insoluble in water. Glue can take the place of gelatin in paulins where the glue-glycerin is used as the inner layer between cloth laminations. Resinous varnish coatings on the outer surfaces of the paulins prevent absorption of liquids by the cloth. The principle involved is obviously applicable to a variety of protective packaging uses.

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## CHAPTER X

### PAPER

THE VALUE of glycerin in the paper-making industry has been recognized for a great many years as witnessed by the numerous references to it in the trade literature and its rather widespread use wherever pliability and strength or special finish is desired.

Connor and Nadelman<sup>1</sup> report in "The Mechanism of Softening Papers" that glycerin is an excellent paper softener even at low humidity. However, they feel that this softening effect does not seem to result from the hygroscopicity of glycerin, but must be the result of other factors under extremely dry conditions.

In a discussion of non-fibrous raw materials for the paper industry, Poor<sup>2</sup> observed that the bulk of plasticizing is being accomplished by the employment of glycerin, invert sugar, and corn sugar or syrup; these materials being used alone or in combination depending upon the results desired. "Efforts to use other agents," he noted, "have been generally unsuccessful, either for economic reasons or non-performance of the material." Poor particularly emphasized the high degree of cooperation between the suppliers of these softeners and the paper mills. This has resulted in an ever-increasing use of plasticizers and a greater number of softened papers that have been well received by consumers.

Glycerin is also used in the manufacture of glassine papers. Without the aid of this agent, the extremely high degree of beating, together with the severe supercalendering under high pressure would result in a very brittle sheet. According to Fries,<sup>3</sup> flexibility is obtained by treating the paper with a plasticizer at one or two stages before it reaches the supercalender. This authority remarks that many attempts have been made to replace glycerin, but that this problem has not been solved satisfactorily.

Glycerin finds similar application, and for like reasons, in the manufacture of greaseproof papers, vegetable parchment, and,

with ever-increasing frequency, in the production of paper toweling, tissues, and kindred products. The recent patent literature presents several instances of such usage. For example, in one quite recent patent,<sup>4</sup> it is specified that paper suitable for towels and the like should be impregnated with glycerin as a softening agent and with a water-insoluble filler, such as magnesium silicate, which is capable of adsorbing and retaining the softening agent in the paper. The proportions used are about 14 to 16 ounces of the filler to about 28 fluid ounces of glycerin.

In another patent,<sup>5</sup> a softening agent for paper products, such as towels or napkins, consists of:

	%
Unreacted Urea .....	20
Glycerin .....	10
Talc .....	10
Water .....	60

Glycerin is a standard ingredient of paper sizing compositions, especially those compounded with rosin and similar materials. An example from the patent literature is illustrative. In this case,<sup>6</sup> use is made of an aqueous sizing dispersion consisting of free rosin soap, a protective colloid and a selected agent, one of which is glycerin. The purpose of glycerin in this composition is to render the dispersion stable to coagulation upon repeated freezings at very low temperatures.

Special coatings and finishes for paper likewise utilize glycerin. One example, given in the most recent volume of the *Chemical Formulary*,<sup>7</sup> shows the use of glycerin in zein (prolamine) paper coatings. Typical is the following grease-resisting coating:

	Parts by Weight
Zein .....	25
Urea .....	8
Glycerin .....	5
Alcohol (85%) .....	100

Particularly important are treated papers suitable for use as food and similar containers. In this connection, it should be remembered that glycerin itself frequently serves as a barrier to oily or greasy substances and to many solvents. Illustrative of such usage is a recent patent<sup>8</sup> for making papers suitable for food

containers by treating the paper with glycerin and one of several stearates, among them glyceryl stearate.

According to an Australian patent<sup>9</sup> for making a pest-resisting agent for use on paper products, sheets of paper or cardboard are coated with a solution consisting of:

	%
Formalin .....	5
Glycerin .....	5
Ammonium Hydroxide .....	2
Casein .....	5
Water .....	83

Several sheets of paper are put together and in between is placed one sheet coated with the above solution, to which is added some blue coloring matter. The resulting laminated sheet is then coated on both sides with another glycerin-containing solution consisting of:

	%
Formalin .....	10
Glycerin .....	2
Boric Acid .....	1
Sulfuric Acid .....	1
Water .....	86

The resulting product is then suitable for manufacture of packing boxes, bags, wrapping materials and related packaging products.

Special treatments for paper containers sometimes utilize the varied properties of glycerin as is illustrated in a patented composition for fiber containers to prevent sticking of asphalt and similar materials.<sup>10</sup> In this case, use is made of substances such as a clay-like filler 40 parts, sodium tetrapyrophosphate up to 0.5%, a size, such as low grade glue up to 2.5 parts, glycerin, as a softening agent up to 7.5 parts, a superficial binder of Sterculiaceae gum 1 part, an alkali carbonate, as a stabilizer 2.5 parts, and water up to 100 parts.

Similarly, sealing compositions for this type of container utilize glycerin in their formulation. Thus, in one method,<sup>11</sup> the metal ends of food containers made from one or more layers of fibrous materials are sealed by means of a highly viscous solution containing:

	%
Barytes .....	10.1
Asbestine .....	5.0
Karaya Gum .....	0.3
Colloidal Clay .....	1.9
Glue .....	4.5
Glycerin .....	2.5
Casein .....	1.8
Ammonium Hydroxide (28%) .....	0.7
Rubber Latex (Solids) .....	2.0
Vulcanized Rubber (Solids) .....	5.0
Water .....	66.2

In the paper laboratory, glycerin still continues to serve an important function as a mountant for the microscopic study of paper.<sup>12</sup> The recent TAPPI Microscopy Committee report<sup>13</sup> mentions Preston's<sup>14</sup> paper on using glycerin and liquid India ink as an imbedding medium for section cutting. The India ink, a dispersion of carbon particles, does not stain fibers and has very great opacity.

A very interesting use of glycerin in paper is as a major constituent of the synthetic alkyd (glyceryl phthalate) resins and ester gums. These glycerin-containing resins have already found extensive application in paper processing and treatments, and new uses are constantly being developed. Sometimes these alkyd resins are used alone in the specialized paper treatments, but more frequently they are used in conjunction with other materials. Thus in one case,<sup>15</sup> use is made of a waxy substance and an ester gum of glycerin and polymerized resin to make waterproofing compositions suitable for paper and other fibrous materials. In another instance,<sup>16</sup> greaseproofing films for paper are made from a base material comprising gelatin or casein, water, ammonia and a partially condensed, soluble phthalate ester formed by heating glycerin and phthalic anhydride under specified conditions.

The distinctive qualities of these various modified alkyd resins have been finding wide utilization in the manufacture of highly specialized paper products. One rather unusual use for one class of alkyd resin is given in a patented procedure for making filter paper.<sup>17</sup> In this case, the fibers of porous paper stock are loosened and distorted by treatment with an alkali, washed and dried to



increase the filtering capacity of the stock. A thin solution of glyptal resin is applied simultaneously and serves both to waterproof the fibers and to cause them to adhere together.

Russian studies<sup>18</sup> on methods of preparing water-resistant polishing paper afford other instances of alkyd utilization. Paper, particularly suited for polishing surfaces prior to lacquering, was developed after numerous tests. The best binder for the requisite abrasive was found to be a synthetic resin; such as alkyd, phenol-alkyd or cresol-alkyd resin. Carborundum was the recommended abrasive and an alkyd-base lacquer was selected for the "fixing" substance.

Water-dispersed special alkyd resins are also used in paper treatment.<sup>2</sup> Alkyd emulsions are available commercially and are used in the impregnation of paper and paper board. According to Maguire and Rote,<sup>19</sup> in a report to the 1942 TAPPI meeting, water-soluble alkyds may prove to be of interest as a beater size for special purposes, since they are readily precipitated by acids. These resins can also be incorporated into casein, starch or glue coatings to improve toughness and adhesion.

The patent literature affords instances of the use of such alkyd resinous preparations. In one recent example,<sup>20</sup> resin emulsions suitable for use in coated papers are prepared from a mixture containing 70–98% of a water-insoluble, drying oil modified alkyd resin together with 30–32% of a rosin-maleic acid resin.

Other glycerin derivatives are finding application in the production of paper specialties. Thus, in the manufacture of a coated paper bag suitable for holding oil for an extended length of time, use is made of paper associated with a relatively non-volatile, oil-resistant softener such as polyglycerin. Polyglycerin prevents the paper from cracking or creasing during manufacture or use.<sup>21</sup>

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## CHAPTER XI

### PHOTOGRAPHY \*

FEW PRODUCTS have been adapted to such a variety of uses in the photographic field as glycerin.

Practically every photographer knows this compound to some extent. Many of its uses, however, pass unrecognized since so many of its most valuable applications are in the manufacture and treatment of the films and sensitive emulsions without which modern photography would be impossible. Glycerin, as such, however, is becoming increasingly utilized directly by expert photographic technicians in producing finished pictures of high order. Also in the newer phases of photography, such as direct color photography and the like, glycerin plays an ever-growing part.

Probably the most important use of glycerin from the picture-taking aspect derives from its hygroscopic properties; that is, its capacity to attract and retain moisture. By this action, glycerin maintains the flexibility and suppleness of films, prints and other materials, thus preventing cracking, brittleness and crumbling. The excellent solvent properties of glycerin may also be advantageously utilized in many photographic processes.

Although the chief use of glycerin in the gelatin, light-sensitive emulsions, whether on film or paper, is as a plasticizing agent, recent work has shown that glycerin combinations have other valuable applications in these layers as well. Steigman<sup>1</sup> points out that hot glycerin has the property of forming sulfur-containing compounds with sulfur-containing chemicals. These glycerin preparations can be used to cause photographic emulsions to ripen rapidly, because of their ability to cause easy formation of silver sulfide nuclei. A Swiss patent describes a very similar process.<sup>2</sup> Here a substance which is useful in preparing photographic emulsions is made by heating a thiosulfate with glycerin. Another

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product for making light-sensitive layers is the photographically active body made by dissolving cystine, a sulfur-containing amino acid, in glycerin by heating.<sup>3</sup> In another process owned by the same company, wool (rich in cystine) dissolved in glycerin is employed in a gelatin emulsion for producing color when developed.<sup>4</sup> Glycerin also serves as an adhesive agent or adhesive ingredient to bond the emulsion layers to the supporting elements.<sup>5, 6</sup>

As a solvent and penetrant for sensitive layers in which the binding agent is a substance other than gelatin, glycerin is definitely useful. This is particularly notable in the manufacture of cellulosic carriers for sensitive materials, a type of carrier material which has proven valuable in color photography. In one patent, in which the colored layer has anti-halation properties, sodium cellulose phthalate is a carrier for crystal violet 6 B, tartrazine, glycerin and saponin. Other similar examples are given in this patent.<sup>7</sup> In another process, light-sensitive dye-derivatives are impregnated, together with glycerin, into cellulose hydrate sheets.<sup>8</sup> Non-cellulosic materials also employ glycerin. Thus a material for use as a coating for printing elements or negatives having a basis of polyvinyl alcohol or its products is treated with glycerin to increase its elasticity.<sup>9</sup>

The photographic diazotype films and papers are also made with glycerin as an essential ingredient. In one procedure, cellulose foil is impregnated with a mixture of diazophenylamine sulfate, glycerin and citric acid. Other glycerin-containing examples are also given.<sup>10</sup> A French process for making photographic diazotype papers and films employs glycerin in the sensitizing bath for the films.<sup>11</sup> Another procedure employs glycerin in the developing material for this type of photographic work.<sup>12</sup>

Although glycerin does not, apparently, enter directly into the wet-plate, collodion emulsions, it is employed in preparations for preventing these collodion plates from becoming horny and brittle when dry. In one example, where this fluid is used as a softening agent, the collodion-silver halide plate is bathed with a solution containing the mercury salt of eosin, glycerin and a large excess of alkali.<sup>13</sup>

Mertle<sup>14</sup> gives another valued use for glycerin, in the prevention of pinholes in wet collodion images. He indicates that the principal cause of these pinholes is dust and suggests that the interior

of the camera and the plate-holder is coated with a thin film of glycerin as a preventive measure. Glycerin does, however, enter into the preparation of the emulsions of collodion printing-out papers. Hopkins<sup>15</sup> gives glycerin formulas for glossy paper and matte paper emulsions.

Supports for the sensitive layers and emulsions usually contain substantial quantities of glycerin, or are treated with this fluid to maintain flexibility and prevent drying. Cellulose acetate films are prepared by immersing cellulose acetate dope, suitably supported, in a coagulating bath containing glycerin, acetone, and methyl alcohol.<sup>16</sup> Cellulose acetate film, known as safety film, is rapidly replacing similar materials made from cellulose nitrate, which is highly inflammable and dangerous. Glycerin-containing resins, generally referred to as "glyptal" resin, are also finding important applications as emulsion carriers or supports. One of these consists of a transparent flexible film produced by the interaction of glycerin and phthalic anhydride.<sup>17</sup> Another important use of these glyptal resins is as a substratum between the support and the sensitive layer.<sup>18</sup> In another case, where the sensitive material uses a monochrome or multichrome screen, the color screen is separated from the emulsion by a varnish layer containing a glyptal resin as one of the chief ingredients.<sup>19</sup> Cellophane, which contains about 17% glycerin, is also finding wide usage as an emulsion-supporting material. Glycerin enters extensively into the composition of most types of cellulosic films.

As has been indicated, glycerin is being found eminently useful in developing and treating color-photographic materials. In one process, in which a set of multi-colored part images of the same subject are super-imposed to register to form a composite picture in natural colors, an appropriate number of transparent, water-permeable, cellophane-type sheets are sensitized with different solutions. While still in the wet condition, the sheets are treated with glycerin to control their contraction upon drying to such a degree that all the component sheets of the set will, when dried, be in the same state of relative contraction.<sup>20</sup> In other methods, glycerin is used in the solutions employed to modify the coloring of the materials. This patent is notable for the claim that the color changes produced are practically permanent, and not affected by sunlight or by hot and cold water.<sup>21</sup>

More important uses of glycerin, however, will be found in the various treatment and developing baths of color processes. In one series of patents, owned by the Eastman Kodak Company, glycerin is used as a loading agent for processing photographic elements of two or more layers containing record images on a single support. The purpose of employing glycerin as such an agent is to control the diffusion of the developing bath or bleaching bath by increasing the viscosity of the bath. Thus a bleaching bath contains glycerin, isopropyl alcohol, hydrochloric acid and quinone, whereas an example of a stop-bath consists of sodium bicarbonate, glycerin and isopropyl alcohol.<sup>22</sup> Similarly the anti-diffusion action of glycerin is employed in fixing and toning baths.<sup>23</sup> Glycerin is also used as an advantageous adhesive between the layers of color-sensitive emulsions. Two films are joined face to face with an adhesive consisting of a glycerin and water mixture. The mixture fills all the surface indentations of the photographic emulsions without substantially separating them. The combined film is exposed, and the films may then be easily separated. The glycerin-water adhesive is easily removed before the films proceed to the next state of treatment.<sup>24</sup>

The average photographer is more interested in glycerin's uses in developing, printing, finishing and retouching processes, than in the technical aspects of its use. One valuable use for glycerin in developing baths is given by de Fero.<sup>25</sup> He points out that the risk of air bells or bubbles adhering to the surface of an emulsion, whether plate, film or paper, can be reduced by decreasing the surface tension of the bath. After trying a series of wetting agents, de Fero found that the addition of 1 ml. to 5 ml. of glycerin per liter of solution was most efficient. In pyro developers, glycerin is added as a preserver and in ferrous oxalate developers it is used as a restrainer.

In printing, glycerin is also applied with advantage. Henley's reference text,<sup>26</sup> gives a "glycerin process" for developing platinum-type prints. By this method, negatives which may have been discarded because of the dim, flat prints which they produce, may be made to yield clear, bright, sharp pictures. By the same method, negatives that are too hard and sharp may be made to produce softer prints. In this procedure, the paper is printed a little deeper than usual. The print is then placed, face up, upon

a piece of clean glass. If the print has a tendency to curl, the glass is moistened with glycerin. Using a broad camel's hair brush, the entire print is thinly coated with pure glycerin. The glycerin is blotted off with special blotting paper in three or four seconds. Those portions of the print which it is desired to restrain or partly or entirely eliminate are recoated. The part of the print that it is desired to develop is now painted with a solution consisting of 1 part of glycerin and 4 parts of normal developer. Those portions should be blotted from time to time to prevent developing too far. Developer, full strength, without glycerin, is used where a definite or deep shade is needed. As soon as any portion of the print has reached the desired degree of development, it should be carefully blotted and glycerin-coated. When the print is developed as desired, it is placed in hydrochloric acid and washed as usual. With this glycerin process not only may valuable subjects be retrieved, but normal negatives can be made to yield artistic, unusual prints.

Hopkins<sup>15</sup> gives a glycerin-containing formula for making platinum paper prints with strong contrast. This is particularly useful in making prints from negatives that are thin and lack density especially from films that have been developed with a metol hydroquinone developer. This special developer consists of:

Potassium Oxalate .....	4 oz.
Sodium Phosphate .....	1 oz.
Hot Water .....	32 oz.
Potassium Bichromate .....	22 gr.
Glycerin .....	2 oz.
Potassium Chloride .....	1 oz.

The mixture is well stirred, used when cold. Stored in an amber colored bottle.

Fixing after the use of this developer is accomplished by the usual hydrochloric acid baths and final washing.

Hopkins also describes methods for local development on bromide paper. Three separate solutions are used: (1) normal, weak developer, (2) 10% potassium bromide, and (3) glycerin. The developer is flowed over the paper until the image begins to appear, the print is then laid on a glass sheet and rinsed in water. Large areas that are to be restrained are painted with glycerin while smaller portions are treated with the bromide solution.

Formalin hardening baths contain glycerin additions to prevent undue brittleness and cracking of the film. One instance from the patent literature aptly gives the use of glycerin in these baths. "This mixture, especially suited for motion picture films, contains formaldehyde to harden the films, tannic acid to render them more resistant, and glycerin to soften them and make them hygroscopic. The sensitive layers on their supports are passed through the usual developing chamber, into the above preparation and then into the regular drying apparatus."<sup>27</sup> Drying combinations sometimes utilize glycerin too. Wet collodial photographic layers, sensitive to hot air, are rapidly dried by a mixture of 60% alcohol, containing glycerin as an added dehydrating substance.<sup>28</sup>

Glycerin enters extensively into the preparation of many compounds for special photographic uses. It is an essential ingredient of masking pastes. These pastes must have a sufficient consistency so that they will not flow down, yet they must not cause breaks or cracks in the film. Furthermore, they must be capable of being brushed on to give clean sharp edges. The proportion of glycerin must be such as to preserve the film from excessive drying. The formula given below meets all of these requirements:

Glycerin .....	1 gal.
Whiting .....	1 lb.
Neutral Soft Soap .....	1 lb.

The glycerin and soap are mixed and the whiting is stirred in.

Other formulas are available but this is the simplest and one of the most effective.

To prevent curling, the following "stay flat" preparation is suggested:

Gelatine .....	60 g.
Golden Syrup (Karo) .....	60 g.
Glycerin .....	60 g.
Chrome Alum .....	1.1 g.
Water, to Make .....	1 l.

The syrup and glycerin are mixed in  $\frac{3}{4}$  of the water, the gelatine is soaked in this mixture for half an hour and then warmed to 120°F. The alum is dissolved in 60 ml. of water and made up to one liter with water by pouring the first into the second. Thirty grams of this will cover 100 square inches. The mixture sets in 24 hours. All the



preparations should be used at the time they are made, since they cannot be remelted.

Photographic prints often have a tendency to curl due to the fact that the treated layer dries faster than the paper. Rubbing the back of these prints with a 10% solution of glycerin and allowing to dry will tend to prevent curling. A similar solution, 1 part of glycerin to 12 of water, will serve this anti-curl purpose if the prints receive their final washing in such a combination. When dried, these glycerin-treated prints will be found to retain their full brilliance, as well as permitting of easier handling and mounting. Pictures wiped or washed with the glycerin-water solutions are less likely to crack or break when the photos are plate-sunk.

Glycerin also enters widely into many touch-up and blackening combinations. Several of these are patented and quite complex, however.<sup>29</sup> A dead black varnish that anyone can prepare and use consists of:

Borax .....	30 gr.
Shellac .....	60 gr.
Glycerin .....	30 min.
Water .....	2 oz.

The ingredients are boiled until dissolved, the solution filtered and to this is added:

Aniline Black .....	120 gr.
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This solution is applied with a brush, and may be repeated when dry if necessary.

A glycerin-containing print varnish should prove useful in many instances. One such preparation consists of:

Borax .....	15 gr.
Pale Yellow Shellac .....	30 gr.
Sodium Carbonate .....	5 gr.
Glycerin .....	15 min.
Water .....	½ oz.

The ingredients are well mixed and shaken. Powdered pumice or whiting is added to precipitate the wax from the shellac and shaken well. The mixture is allowed to stand for two or three days and then decanted and filtered.

A hypo-glycerin photographic stain remover given by Hopkins can be prepared by mixing:

Hypo .....	1 oz.
Water .....	1 oz.—and then adding
Glycerin .....	1 oz.

This solution is painted over the dry negatives and left on for 12 hours.

A stripping solution for use on gelatine negatives consists of:

	Parts by Weight
Methylated Spirit .....	25
Water .....	1
Glycerin .....	1

Just prior to the use of this stock solution, hydrochloric acid, 6 to 30 drops per ounce, is added.

Although glycerin is a standard ingredient of photographic mounting pastes and adhesives, where its hygroscopic action prevents curling, shrinking and peeling of the mounts, the following transparent cement for photographs should prove valuable. By means of this adhesive it is possible to mount pictures, face up, directly upon the glass. It consists of:

	Parts by Weight
Glycerin .....	4
Best Selected Gum Arabic .....	4
Powdered Gum Tragacanth .....	1
Distilled Water .....	32

The tragacanth is dissolved in half the water, the gum arabic in the other half. The solutions are mixed, the glycerin incorporated and again mixed thoroughly. The gum arabic should be of the best grade. If the preparation is not as clear as desired, it may be filtered through absorbent cotton.

The utility of glycerin extends even to the taking of photographs. Everyone knows that drops of glycerin are used to simulate tears in taking motion pictures. The same idea is applicable to create the illusion of perspiration, water droplets, spray and the like. Since glycerin does not evaporate, its use is advantageous, particularly where heat is generated, as under flood lights and the like. High-lights can be brought out when photographing fruits, vegetables, porcelain and a host of other objects, by coating

with a thin film of glycerin. The fact that glycerin may be readily removed from these objects by the simple use of water is also a considerable factor. In cameras, where a ground-glass is used for focusing, when it is necessary to make extremely sharp pictures, glycerin is useful. A small spot is made on the matte side of the ground-glass with glycerin. Focusing is done on this spot. This process is especially useful when focusing near-by objects and where the depth of focus is small.

Of course, such a brief review can hardly hope to cover the many uses of glycerin in photography. For instance, no mention has been made of the use of glycerin in making projection screens which also serve as sound diaphragms,<sup>30</sup> or, its employment in making paper for protecting photographic films,<sup>31</sup> or, in making photographic paper negatives,<sup>32</sup> or, in transferring photographic prints.<sup>33</sup> Many other instances could be cited. In this study, however, many uses of glycerin, taken from recent patent and other literature, indicate its versatility and adaptability in every phase of photography and point the way to still broader utilization.

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## CHAPTER XII

# PLASTICS

MENTION GLYCERIN to the plastics chemist and his first thought is of alkyd resins. There is a growing awareness of the value of glycerin-containing resins, not only in protective coatings, but also in molded products. Glycerin itself is finding ever-increasing use as a plasticizer for plastic materials and molding fillers.

Practically, the industrial history of the alkyds actually looks back only about twenty-five years, and its large scale utility is only a little over a decade old.<sup>2</sup>

Although, as pointed out by Hovey and Hodgins,<sup>1</sup> literally thousands of alkyd compositions have been described in the literature, relatively few of these compositions, by comparison, depart far from the use of glycerin, phthalic anhydride, and oil derivatives. Without going into further details, since these have been reviewed in previous discussions,<sup>3, 4, 5</sup> it may be said that the alkyd resins are made up of various mixtures of polybasic acids, polyhydric alcohols and suitable modifying agents. Through judicious selection of the raw materials, the final condensation product can be one that will possess the proper color, drying rate, viscosity, durability, pigment-retention, adhesion, toughness and other requisite qualities. The use of glycerin, with its three hydroxyl groups, is most advantageous since it provides far more cross linkages and the formation of three-dimensional molecules of greater complexity, durability and drying rate. An increased number of carbon atoms in the polybasic portion results in a tougher and more durable product. Phthalic anhydride is most generally employed (e.g. glyceryl-phthalate resins), but other acids such as maleic, succinic and sebacic are finding increasing use.

The resulting alkyd resins find their most important application in paints, lacquers, varnishes, enamels or other coatings for many types of materials requiring protective finishes. Necessary modifications for specific uses are obtained by varying the modifying

agent, which is usually an oil, fatty acid, or, natural or synthetic resin.

Beaman<sup>6</sup> remarks about the alkyds: "Possessing an inherent beauty all their own, the alkyd resins also have such outstanding characteristics as toughness, flexibility, and color retention and can withstand high baking temperatures without experiencing any undesired results. They are adaptable to practically every phase of coating where superior qualities are essential to provide protection from wear, tear and the elements."

According to Wakeman and Weil,<sup>7</sup> alkyds have become indispensable in the formulation of synthetic coatings. In combination with nitrocellulose and phenolic or urea resins, they find extensive application in quick-drying interior finishes, in automobile and refrigerator lacquers and enamels and now in all manner of coating materials for the army and navy.

The ability of the glyceryl phthalate or alkyd resins to meet tough requirements and their value in aircraft finishes has come in for special commendation<sup>8, 9</sup> both from paint experts<sup>10, 11</sup> and government authorities.<sup>12</sup> Answering the question why so many government specifications are predicated on glyceryl phthalate resins, Reizenstein<sup>13</sup> has declared that on the basis of speed of application, durability and performance, the alkyds have been shown to be the most effective coatings that could be used.

The why of alkyd resins in specification finishes has been well summarized by Glaser:<sup>14</sup> "Alkyd resins provide the paint formulator with an excellent and most versatile group of tools with which to prepare suitable finishes for war time and for peace time as well. The wide acceptance of alkyd-resin finishes by the government agencies, after long study, indicates that without much doubt, in most cases, these coatings provide the optimum combination of properties for the largest number of protective, decorative and camouflage coatings. Finishes made from the proper alkyd-resin bases possess excellent adhesion to most surfaces, good color retention and excellent weathering characteristics. They have hardness, flexibility, moisture and solvent resistance. They withstand the action of many reagents and show little change in gloss, even after long exposure periods. Many require reduction with only inexpensive thinners."

Far from being content with progress already made, resin

chemists have continued to develop new and improved alkyds.<sup>1, 15, 16, 17, 18, 19, 20, 21, 22</sup> An interesting development of the last few years has been the growing utility of "water" or emulsion paints; a good proportion of which are essentially dispersions of alkyd resins. According to Pearce,<sup>23</sup> alkyd resin emulsion paints are more satisfactory than oil and quick-drying varnish types for porous surfaces, and these emulsions have found wide use in increasing quantities in interior wall paints and exterior paints for cement, concrete, cinder blocks and similar surfaces. Their quick-drying qualities and freedom from paint odors make them especially suitable for hotel, apartment and other residential painting.

Singularly enough, alkyd resins in water dispersion have been known for some years.<sup>2</sup> However, a new interest in these products has arisen,<sup>24</sup> as a great number of patents was granted for such compositions.<sup>25, 26, 27, 28</sup>

Noteworthy, too, is the growing utility of these glycerin-containing alkyd resins in connection with other standard<sup>29, 30</sup> or newly developed<sup>31</sup> resinous materials. The urea-formaldehyde-alkyd resin combinations are being widely used, not only in white baking enamels but also for colored enamels because of the short baking period necessary to make them extremely hard, marproof, and light-fast.<sup>32</sup>

In the past, alkyds have not found extensive use in molded products, but the more recent patent literature indicates a modification of this view. For example, one alkyd resin composition suitable for both molded products or coatings is mixed with hexamethylene diisocyanate to effect more rapid drying.<sup>33</sup> Another composition, designed for similar double utility, is formed by heating maleic acid and a compound, such as oleic acid, until reaction between the acids is effected. Glycerin is then added to the mass and the heating is continued to cause a reaction between the acidic and the hydroxyl groups.<sup>34</sup> There are other instances of such alkyd resin usage for molding, coating or impregnation.<sup>35, 36</sup>

Alkyds, in conjunction with other resins, are finding use in the formulation of thermoplastic synthetic compositions.<sup>37</sup> Of particular significance is the conjunct use of urea-formaldehyde resins with glyceryl phthalate resins for making heat-convertible molding compositions.<sup>38</sup> One patented process uses a combination of such resins to form cast products which are clear and colorless.<sup>39</sup>

The alkyds have excellent binding properties, but their slow conversion has been a factor against their wider use. Nonetheless they have found extensive use as binders for mica to produce insulating materials of high electric strength and for laminating a wide variety of materials.<sup>2</sup> The excellent bonding properties of these resins has been finding new applications, especially in the manufacture of abrasive sheets.<sup>40, 41, 42</sup> Also in preparing plastic compositions, as in the following material described in a British patent.<sup>43</sup>

	%
Cork Powder .....	52.0
Asbestos .....	3.0
Slate Powder .....	8.0
Natural Resin .....	5.3
Naphthenic Acid .....	5.0
Sodium Hydroxide .....	0.7
Casein .....	12.0
Glycerin Resinate .....	8.0
Natural Resin Modified-Glycerophthalic Resin .....	6.0

With an already established place in coating compositions for textiles, paper, leather and the like, the alkyd resins have found increasing employment in many new specialty finishes for textiles.<sup>44, 45, 46, 47</sup> In his discussion on plastic coatings for textiles, Cleaveland<sup>48</sup> has listed the properties which make the alkyds preeminently suitable for such purposes. In the meantime, these resins have already proved their worth in processes for making fabrics transparent and impermeable to fluids,<sup>49</sup> for imparting high insulating qualities<sup>50</sup> and other modern treatments.

Alkyds (e.g. "glyptal" resins) have come to the rescue in the production of substitutes for "oiled" silk, needed in wound dressings,<sup>51</sup> and in bolting cloths, required in the shifting and sieving of fine powders.<sup>52</sup> Dispersions of alkyd resins have been used also in newer processes for coloring textiles.<sup>53</sup>

In addition to these more recent applications, the glyceryl-phthalate resins have been used in other phases of modern industry. Thus, alkyds have been employed in making printing inks,<sup>54</sup> in special coatings for glass<sup>55</sup> and in processes for coating objects with glass,<sup>56</sup> in container-sealing compositions,<sup>57</sup> and in the production of films for color photography.<sup>58, 59</sup>



Glycerin itself finds many uses in connection with plastics and their formation into molded objects. Because of its excellent heat-transmitting properties, it is often used in the immersion baths for forming acrylic plastics. Thus it finds use in shaping acrylics for bomber noses<sup>60</sup> as well as for forming artificial dentures.<sup>61</sup> As a pressure-transmitting fluid, glycerin is often employed in hydraulic equipment. In one recent patent,<sup>62</sup> for example, a process is described for molding optical lenses or the like from the thermoplastic materials under equalized pressure. Glycerin is specified as being suitable for use as the pressure-equalizing medium.

More important, however, is the wide use of glycerin as a plasticizer for various plastic materials. For example, for blood compounds containing urea-formaldehyde resins,<sup>63</sup> for phenol-formaldehyde resins,<sup>64</sup> for fibrous cellulosic materials,<sup>65</sup> and for hydrolyzed wood.<sup>66</sup>

This chapter should not close without citing the frequent use of glycerin as a plasticizer for various polyvinyl compounds now finding extensive application in many phases of modern industry in the form of molded products, films, impregnating compositions and as laminating agents.<sup>67, 68, 69, 70</sup>

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## PRINTING AND LITHOGRAPHY

GLYCERIN is a familiar compound in the realm of printing. It plays a part not only in the formulation of composition rollers, but in many other compounds required in printing. Thus glycerin enters into the preparation of printing blankets, printing matrices, in the preparation of printing plates, in specific printing processes where certain results are desired as in photo gelatin processes and in the manufacture of printing inks and pastes. In these varied uses, not only is glycerin itself widely employed, but its derivatives, more especially the synthetic alkyd resins, have likewise come into application.

Undoubtedly the most important property of this clear, heavy, syrupy liquid, from the standpoint of the printer, is its hygroscopicity. Through this ability to attract and retain essential moisture, glycerin helps to prevent excessive drying that will result in cracking, crumbling and eventual disintegration. For example, the ability of glycerin to absorb moisture and keep a roller tacky is considered one of its chief advantages in composition roller making, though this property is hardly limited to rollers of this type. Through this hygroscopic property, glycerin likewise helps to retain the essential resiliency so necessary for good printing rollers. Moreover, because of its high boiling point, glycerin "stays" put even under wide variations of temperature.

From the printer's standpoint, the most important use of glycerin is in the preparation of glue-glycerin composition rollers. It is generally conceded that a major step towards fast modern printing was the development of power-driven, cylindrical rollers, made of glue and glycerin, which carried the ink in smooth distribution to the type.<sup>1</sup>

These composition rollers are made of glue and glycerin, plus a small proportion of other ingredients, some of them supposedly the secrets of individual roller manufacturers. The use of such

ingredients, generally claimed to give superior properties to rollers, are patented.<sup>2</sup> Methods for applying the glue-glycerin compositions have also been patented.<sup>3</sup> In general, however, the procedures for making the compositions and shaping them into rollers are used by all manufacturers of such equipment.

The compound is usually made by softening high-grade glue or gelatine in water and gradually heating. The glycerin and other ingredients may be added to the water prior to adding the glue or these ingredients may be added after the soaked glue has been carefully heated. Often, a setting agent, either formaldehyde or a chromate salt, is incorporated into the mixture to insolubilize the glue. The molten mass is then poured into roll molds around a suitable core, and on cooling, sets to form a composition having a rubbery consistency. The proportions of glue and glycerin are not fixed, however, but are varied according to the atmospheric conditions under which the roller is to be employed. Temperature and humidity are prime considerations in the formulation of a glue-glycerin roller composition. Although the terms "winter" and "summer" rollers are generally used, Trotter<sup>4</sup> feels that such rollers should really be renamed "warm weather" and "cool weather" rollers because the weather man is notoriously ignorant of calendars.

As illustrative examples of glue-glycerin compositions three different formulas<sup>5</sup> are given in the following:

	I	II	III
	Parts		Parts
	by Weight		by Weight
Hide Glue .....	1	10 lb.	30
Glycerin .....	1½	12 lb.	65
Sugar .....	½	10 lb.	..
Water .....	1	sufficient	60
Borax .....	..	..	1
Isinglass .....	..	1½ oz.	..

Of course, numerous other formulas for making such compositions, using other special-purpose ingredients in addition to the glue and glycerin are available in the technical and patent literature.

An advantage of such compositions, in addition to their superior inking qualities, is the fact that they can be remelted and used

again and again. Very often the remelted compositions can be incorporated with fresh materials, as in the following example<sup>5</sup> for a printer's roller composition:

Glue .....	100 lb.
Water .....	3 gal.
Glycerin .....	300 lb.
Old Roller Stock .....	200 lb.

Even when the roller composition reaches the stage where it can no longer be reused, a large proportion of the valuable glycerin can be recovered and used again. Because the glycerin is fully soluble in water, straight water extraction processes may be employed with subsequent separation and purification.<sup>7</sup> By another process, the cut-up rollers are distilled with steam at 165°–200°C. to recover the glycerin.<sup>5</sup>

Also in the composition glue-glycerin classification are the so-called “non-meltable” rollers.<sup>4, 8</sup> In addition to the usual glue and glycerin constituents, these rollers contain other ingredients which help to prevent their wearing down under the influence of high-speed presses and make them less amenable to weather changes. Although such properties are obtained only at a sacrifice of some printing quality, these rollers do possess most of the printing-quality advantages displayed by the regular composition rollers. When composition rollers are required on speed presses, because of the superior quality obtained, the non-meltable rollers have given satisfactory results.

Coated rollers likewise utilize the advantageous properties of glue-glycerin compositions.<sup>9</sup> Although their initial cost is higher, it is generally believed that such rollers are somewhat less expensive in the long run.<sup>8</sup>

The proper care and maintenance of glue-glycerin composition rollers, no matter what the type, is a prime consideration, not only from the standpoint of printing quality but also from the economic aspect. The subject has frequently been discussed in the technical literature.<sup>4, 8, 10</sup> Cleanliness, proper storage and proper setting are all essential considerations. Selection of the cleaning solvent is important and should meet the requisities of each type of roller. Some appropriate advice along these lines has been aptly summarized by Colehower:<sup>11</sup> “The use of volatile substances such

as gasoline, alcohol and quick evaporating cleansers should be avoided on any type of roller as they are injurious to either composition or rubber. Water should be kept from composition rollers and when not in use, they should be stored in a cool, dry closet; making sure that no mice or bugs can reach them, for the glue and glycerin combination in composition rollers is a tasty meal for rodents."

The employment of glycerin is not limited, however, to composition rollers. It is also used in making rubber rollers or in formulas where rubber is an essential ingredient.<sup>5, 12</sup> The chemical properties of glycerin are also brought into play in the production of modern synthetic resin rollers, made with alkyd resins. Alkyd resins, in general, may be considered the reaction products of glycerin and phthalic anhydride or related chemical compounds. Since these resins can be so controlled or so modified as to meet an almost infinite variety of requirements, it is not at all surprising that certain of these alkyd resins should have been prepared to meet the needs of printing roller manufacturers. Such resins are now being used to produce printing rollers that will maintain a constant degree of softness and yet not lose their shape during a year or more of constant use. Moreover, they are not readily affected by temperature changes.<sup>13</sup> Processes for making such rollers are generally patented.<sup>14</sup> The patent literature also reveals that special glycerin-formulated alkyd resins may also be applied over layers of vulcanized rubber to give improved properties to the rollers.<sup>15</sup>

At least one mechanical unit is available which sprays a vaporized solution of three ounces of glycerin in a quart of water above printing rollers. It is claimed that this glycerinized vapor acts as a local humidifier designed to lengthen the life of rollers, keep them tacky, cut down on excessive ink consumption, increase press production through fewer stops, and improve printing quality. These advantages of the glycerin spray are said to be applicable to all types of letterpress printing rollers whether composition, non-meltable, rubber, synthetic or process.<sup>16</sup>

Glycerin is used as a plasticizer for the bonding agents employed in making printers' blankets. Glycerin derivatives and glycerin-containing resins are also used in conjunction with basic components of this type of printing requisite.<sup>13, 17, 18</sup> The prepara-

tion of printing matrices likewise utilizes the several advantageous properties of glycerin—a fact clearly evidenced by the patent literature on the subject.<sup>19, 20, 21, 22</sup>

Lately glycerin has come into fairly wide use in electrolytic processes for preparing printing plates.<sup>23</sup> Thus, for the electrolytic zinking of offset plates, one foreign authority<sup>24</sup> recommends that the printing surface be etched with a 3% hydrochloric acid solution in glycerin for the photo-mechanical process and then plated from a bath containing 300 g. of zinc sulfate (goslarite), 30 g. of ammonium chloride, 15 g. of sodium acetate, and 120 g. of glucose per liter, the current density being varied during the course of the process. Then the plates are prepared for printing in the usual manner, the relief being removed by anodic etching.

Glycerin enters frequently into printing plate etching processes, more especially as a constituent of special plate resists.<sup>25, 26</sup> It might be mentioned that in the film dot etching process, the inclusion of glycerin with the hypo solution not only serves to retard the action of the ferricyanide but also largely prevents the crystallization of the hypo.<sup>27</sup>

As might be expected, the hygroscopic properties of glycerin find extensive application in photo-gelatin printing processes which still are widely employed to secure fine detail in high quality printing and lithography.<sup>28, 29</sup> Of the several processes employed, perhaps none gives such excellent photographic details as does the old collotype process.<sup>30, 31</sup> In this procedure, bichromated gelatin plates mounted on glass rather than a lithographic stone or metal plate are used as the printing surface. The plate is exposed under a photographic negative, the negative becoming waterproof where the light penetrates through the negative, but remains soluble in varying degree according to the amount of light penetration. After washing out the surplus bichromate, the plates are "etched" with a solution of glycerin in water which swells and moistens the unhardened areas according to the degree of light exposure. Printing is done on flat-bed lithographic presses. From time to time fresh applications of the glycerin solution are made to prevent drying out of the plate and subsequent loss of detail. Collotype printing may also be done in colors. There are several modifications of this process and the patent literature also presents photo-gelatin processes that utilize glycerin.<sup>32</sup>



It should also be mentioned that glycerin is used in silk screen printing or stencil screen reproduction work, e.g., in making silk screen stencil fillers,<sup>5</sup> and also in the photographic procedures (essentially gelatine processes) employed in these methods.<sup>33</sup> Glycerin is also employed in Vinyon,<sup>34</sup> the silk screen substitute.

Glycerin and its resinous alkyd derivatives find use in the formulation of a wide variety of printing inks and pastes.<sup>35</sup>

Before concluding this brief discussion, mention may be made of two comparatively minor uses of glycerin, which nevertheless contribute considerably to printing efficiency. One is the use of glycerin for moistening the finger tips when feeding paper into a press and in gathering the forms prior to covering them. Used this way, glycerin facilitates handling the paper without staining. Various ingenious devices have been suggested to aid in moistening the fingers, among them being the use of a glycerin-soaked sponge in a wrist holder, or the use of a cut-off oil can with a glycerin-wet piece of cotton in the opening.<sup>36</sup> In general, however, a cloth or sponge near at hand will suffice to wet the fingers, as needed.

The other application of glycerin concerns its value in preventing the accumulation of electrical static which holds sheets of paper tightly together and thus slows work. Rubbing glycerin on packing and tape has been suggested as one helpful means of preventing static and curing offsetting.<sup>37</sup> In one plant (using Miller heads), static was eliminated and speed almost doubled by placing a glycerin-saturated cloth on the main shaft above the paper truck and allowing it to dangle from  $\frac{1}{4}$  to 1 inch from the top sheet on the stock pile. It was suggested that the same procedure could be applied on any press where a cloth can be placed near the sheets being drawn into the bed.<sup>38</sup>

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## PAINTS AND PROTECTIVE COATINGS \*

IN THE revolutionizing of the paint and varnish industry brought about by the introduction of modern synthetic resins with their far reaching possibilities of adaptation and application, glycerin, as a constituent of the alkyd resins, plays a major role. These glycerin-containing resins represent one of the chief scientific advances of the last few decades, and, by their use, the industry has today a widely broadening choice of basic materials.

Old methods and the employment of natural materials are now almost completely displaced by products from the scientific laboratories of the world. According to one government publication on the subject,<sup>1</sup> the first departure from these older, traditional practices was the introduction of nitrocellulose lacquers. The second was the application of the alkyd resins, the use of which is increasing rapidly. These alkyd resins are essentially condensation products of glycerin and organic acids;<sup>2, 3</sup> to which are added various modifying substances that help create the specific properties desired. Among the various polybasic acids combined with glycerin to form these resins, phthalic, maleic, succinic and sebacic acids are the most important. Of these, phthalic acid ranks first, and it should be pointed out that at the time when cheap solvents and phthalic acid was also greatly decreased as a result of newly developed processes. Ready commercial availability of the raw materials, glycerin and phthalic acid, stimulated research on these alkyd resins and paved the way for new and unsuspected fields of usefulness.<sup>4</sup>

Although the applications of glycerin are extremely varied and fit into the requirements of almost every modern industry, the most important present-day utilization of this versatile fluid is in the manufacture of alkyd resins and ester gums, both groups of which products are indispensable to the paint industry.<sup>1</sup>

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As pointed out by Fitzpatrick,<sup>5</sup> the paint trade is interested only in varnishes and resins that are initially soluble, that are capable of being handled and when properly treated are convertible into relatively insoluble and infusible forms. "This conversion," says he, "must be two-fold, it must occur on air-drying and also on baking, although not necessarily must the same resin be capable of both. Modified alkyd resins supply these features. They are essentially the compounds resulting from the esterification of glycerin with monobasic and dibasic acid in molecular proportions."

When used in baking finishes these glycerin-containing resins are noteworthy for such qualities and characteristics as great toughness, durability, adhesion, gloss retention, paleness and pigment-binding properties. Air-drying resins possess similar qualities but in a lesser degree, and constant research is continuously improving the characteristics of these products. Combined with nitrocellulose lacquers, an important use for the alkyd resins, these lacquers retain most of their desirable drying qualities, whereas the glycerin-containing synthetics greatly increase the fullness, gloss and durability of the protective coatings.

The history of the alkyd resins may be traced back to 1847, when the great chemist, Berzelius prepared a resinous compound from glycerin and tartaric acid.<sup>6</sup> Others,<sup>1, 7</sup> however, set the date as 1856, when Von Bemmelen described a process by which he had obtained vitreous resin-like materials by heating glycerin with citric acid or succinic acid. All authorities on the subject agree, however, that the real start of research on the alkyd resins began late in 1901. At that time, Smith<sup>8</sup> while studying phthalein dyes, heated glycerin with phthalic anhydride, and obtained perfectly transparent and refractive substances which he suggested as useful cements for ceramic wares.

Research on these glycerin-phthalic acid resins continued, the most outstanding work being that of the General Electric Company during the period 1910–16. Others took up the study, variations were developed and literally hundreds of patents were granted.<sup>1</sup> The true commercial production and utilization of these resins did not really begin, however, until after 1922 when the lowered price of phthalic acid made its use in the manufacture of resins practical.<sup>4</sup> Some idea of the rapid growth attained by the alkyd resin industry is indicated by the fact that in 1929 there

were only three producers of these synthetics in this country, in 1933 only six, but in 1937 this number jumped to thirty-nine.<sup>1</sup>

Another index of the tremendous growth and importance of the alkyd resins is given in government statistics<sup>1, 9</sup> on production during the last several years. The number of pounds produced per year is given in the table following:

Year	Pounds Produced
1933 .....	9,930,705
1934 .....	15,219,248
1935 .....	34,312,713
1936 .....	46,952,452
1937 .....	61,254,019
1938 .....	40,996,727
1939 .....	76,471,640

These figures are indeed impressive and, with the exception of the fall-off in 1938, show the constantly growing demand for these resins. In 1939 the forward progress was more than ever strongly resumed when alkyd resins showed an increase of 87% over the previous year. In the short period of six years the production of these important resins has increased more than eight-fold. This is readily understandable when it is remembered that these glyceryl phthalate resins "have excellent wearing qualities, retain good appearance, can be applied easily, adhere to metal and dry quickly."<sup>10</sup>

Several classifications of the alkyd resins are available, most of them quite practical. One system, that of the government publication on the subject,<sup>1</sup> divides these glycerin products into six groups: 1. Drying alkyd resins; 2. Semi-drying alkyd resins; 3. Non-drying alkyd resins; 4. Miscellaneous modified alkyd resins; 5. Alkyd resins in water dispersion, and 6. Alkyd resins in molding compositions. The first class of alkyds is further subdivided to include such resins as: a, unmodified; b, modified with natural materials; c, modified with other synthetic resins, and d, modified with other synthetic resins and oil extended. This quite inclusive classification gives a good indication of the wide ramifications and ready adaptability and usefulness of these glyceryl phthalate-type resins.

Most of these varied alkyd resins are available under many trade names. Their manufacturers are among the leading chemical producers of this country, and their listing includes such names as

Amberlac and Aquaplex (Rohm and Hass); Beckosol (Reichhold Chemicals, Inc.); Dulux (duPont); glyptal (General Electric); Lewisol (J. D. Lewis, Inc.); Paraplex (Rohm and Hass); Rezyl and Teglac (American Cyanamid & Chemical Co.) and Rauzone (U. S. Industrial Chemicals Co.). Each of these trade names, and many more, identifies a series of alkyd products, each with its specific claims and uses.

Progressive study is steadily widening the horizon of these glycerin-phthalic acid resins. One comparatively recent advance is the creation of emulsions of alkyd resins for use in clear and pigmented coatings. Such products, to be diluted with water at the time of use, are applied by brushing or spraying like other water paints, but have the durability, washability and hardness of oil paints, and compared with oil paints give better coverage, are easier to apply and what is very important, cost much less.

The adaptability of the alkyd resins for outdoor use, even under severe weather extremes, has been recently demonstrated at the New York world's fair. Using the alkyd resins, glyptal, the copper on the exterior of the General Electric building was so well protected that not only did the metal retain its brilliant luster and color, but maintained them during the natural exposure without spotting or turning green.<sup>11</sup>

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## CHAPTER XV

### RUBBER

THE MARCH of events has made profound changes in the rubber picture. Despite these changes, and in many instances because of them, glycerin has continued to find interesting and important applications in connection with both natural and synthetic rubber and rubber compositions. As in the past,<sup>1, 2, 3</sup> glycerin has been employed in newer rubber treatments, rubber-containing compositions, lubricants and substitutes, and more recent conditions have stressed the value of glycerin in rubber conservation methods.

In 1938 Thiollot<sup>4</sup> presented evidence of the advantages of glycerin as a vulcanizing medium. More recent Russian investigations<sup>5</sup> have tended to confirm these findings. In an experimental plant, galoshes were preformed, locked in molds after pressure had been applied, and immediately immersed and cured in glycerin. Comparative physical tests showed that the glycerin method is as good as, or better than, curing under pressure in steam presses. According to the report, the process has possibilities of being made continuous.

Glycerin is recognized as an effective softener and tackifier in the compounding of rubber latex, but it has a disadvantage in that it may be washed out.<sup>6</sup> Its plasticizing action, nevertheless, has proved of definite value in the fabrication of paper carriers for tacky rubber.<sup>7</sup>

Special coatings and other treatments for rubber have long taken advantage of this versatile compound. As synthetic rubbers began to find more widespread use, glycerin was retained in the treatments of these newer materials. Thus, Russian workers found that compositions containing casein, petrolatum stearine, glycerin, ammonia and formalin proved very satisfactory for finishing synthetic rubber substitutes for fancy and saddle leather.<sup>8</sup>

A similar American preparation <sup>9</sup> for finishing synthetic rubber, consists of:

	Parts by Weight
Casein .....	60.0
Petrolatum .....	6.0
Stearic Acid .....	10.0
Glycerin .....	40.0
Ammonia .....	3.6
Formaldehyde .....	9.0
Water .....	Sufficient Quantity

There is a growing utility for the glycerin-containing alkyd resins. These synthetic resins can be modified in a variety of ways to meet some of the needs of the rubber industry. In a typical instance derived from a foreign patent <sup>10</sup> the permeability to gas of hot-vulcanized rubber, especially rubber tires, is increased by treating the surface with a solution containing an alkyd type resin, gelatin and glycerin. Nearer home is a patent covering a series of compositions suitable for coating rubber surfaces. According to this American patent,<sup>11</sup> use is made of a cellulosic derivative, a urea-formaldehyde resin and a soft compatible alkyd resin.

Rubber-utilizing compositions also take advantage of the plasticizing effects of glycerin. Thus, a sealing composition for composite containers for packaging foods may be prepared, according to a British patent,<sup>12</sup> from:

	%
Barytes .....	10.1
Asbestine .....	5.0
Karaya Gum .....	0.3
Colloidal Clay .....	1.9
Glue .....	4.5
Glycerin .....	2.5
Casein .....	1.8
Ammonium Hydroxide (28%) .....	0.7
Rubber Latex (Solids) .....	2.0
Vulcanized Rubber Latex (Solids) .....	5.0
Water .....	66.2

Plasticized polyvinyl alcohol products compounded with synthetic rubbers may also make use of glycerin in the production of



a variety of films, molded articles, textile impregnants, etc. In an example cited in the patent,<sup>13</sup> polyvinyl alcohol resin in the form of a film containing 57% of the resin and glycerin as the plasticizer is macerated with 10 parts of Perbunan to obtain a product in which the buna rubber is uniformly dispersed and its particles covered with a film of the resin.

To reinforce inner tubes for tires, according to one patent,<sup>14</sup> a fluid-sealing material, such as latex, wheat flour and glycerin, is introduced into the tube. In this connection, mention should be made of glycerin for treating tire cords. In one instance, cords, such as those formed of regenerated cellulose, are treated with a hygroscopic liquid, like glycerin. Such treatment, it is claimed, improves the strength of the cords.<sup>15</sup>

Glycerin, alone or in simple combination, is an excellent lubricant for rubber surfaces. It has long been one of the most efficient lubricants for making molded rubber goods. In one British process<sup>16</sup> for making thin-walled rubber articles, a mold is coated with an agent that will not coagulate rubber, such as glycerin in alcohol. After the volatile solvent has evaporated leaving a film of lubricating glycerin, the mold is dipped into a rubber suspension. Then, while still rotating, the mold is pulled out and the rubber coagulated by a jet of steam and subsequently the rubber object is vulcanized.

Simple mixtures of glycerin and alcohol have long been recommended as effective and safe lubricants for rubber shackles and parts of automobiles. Newer technological processes based on the use of rubber also employ glycerin for these purposes. One such, for casting low-melting point alloys in rubber molds, utilizes glycerin as the separating or "anti-stick" agent during the production of the rubber forms used in shaping the metal articles.<sup>17</sup>

Widely used, simple combinations for lubricating rubber surfaces are made by suspending colloidal graphite in glycerin.<sup>18</sup> One of the leading producers of colloidal graphite, in a leaflet explaining the advantages of glycerin in their product (Glydag), points out that the glycerin content: (a) Prevents quick drying, (b) keeps lubricated parts moist and free from squeaks, (c) lowers the freezing point, thus allowing efficient cold weather use, (d) increases viscosity, adding to the ease of application, and (e) increases retention of the graphite on the lubricated parts.

Glycerin plays an essential part in the conservation of rubber articles. One accepted procedure for industrial plants is the addition of glycerin to the water used to rinse the rubber parts of goggles and respirators after sterilization in formaldehyde fumes.<sup>19</sup> This, it will be recognized, is but an extension of the wide use of glycerin to maintain the flexibility, resilience and gloss of rubber items.

Early in 1942 a process was devised by S. D. Lesense of Oklahoma City University for extending the useful life of rubber tires. According to a statement released at the time, the procedure required that the tire be rubbed vigorously with a glycerin-saturated rag, then powdered sulfur rubbed over the surface of the rubber. The glycerin serves to preserve the elasticity of the rubber and the sulfur provides a glossy insulating finish. For best results, it was recommended that the treatment be given twice monthly.

Despite the known fact that glycerin is an extremely critical item in Germany, a note in *Foreign Commerce Weekly* for December 11, 1943, tells that, in the cleaning of articles in which rubber is bonded to metals, Nazi authorities suggest the use of a glycerin-spirit mixture in equal parts. Other details of rubber care, as advocated by the Germans, is included in the published items.

The difficulty of replacing airbags used in tire retreading and tire repair work has put emphasis upon proper care of these critical rubber items. To extend their usefulness, the Rubber Manufacturers Association<sup>20</sup> has made a series of recommendations. The organization points out that, after fifty cures, the inner lubricant, glycerin, usually has been dissipated and should be replaced. If this is not done, the inner lining dries, will crack through the fabric, and will be easily blown out. In the opinion of the Association, this lubricant lack probably causes more airbag failures than any other factor. More recently, the Association suggested the addition of glycerin once a week to keep the inside of the bags soft and pliable.<sup>21</sup>

Glycerin does not find extensive use in the formulation of synthetic rubbers. However, glycerin has an important place in the formulation of many valuable rubber substitutes for use under a variety of specific conditions.<sup>22</sup>

A French method<sup>23</sup> for making plastic and elastic materials capable of being vulcanized involves the formation of glycerin as an integral part of the process. In an example, castor oil is subjected to hydrolysis and cracking in vacuo with the formation of undecylenic acid and glycerin. The glycerin by dehydration gives acrolein, which by hydrogenation yields allyl alcohol. The undecylenic acid is then treated with the allyl alcohol so formed and the ester is polymerized in the presence of catalysts.

Less complex is a rubber substitute patented by an American inventor.<sup>24</sup> The elastic composition, which can be used as a substitute for natural rubber in various applications, is made by mixing and heating the following ingredients:

Gluten .....	12 oz.
Spirits of Turpentine .....	100 ml.
Sulfuric Acid .....	28 drops
Glycerin .....	100 ml.

The resulting elastic rubber-like composition can be vulcanized like the natural product to any desired degree of hardness and toughness.

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## TEXTILES AND DYES

GLYCERIN AND its derivatives are widely used in the textile industry.

In fabric printing, for example, where glycerin is used in the formulation of printing pastes for all classes of dyestuffs and related materials <sup>1</sup> its hygroscopic properties receive first emphasis, but one cannot overlook the solvent and penetrating action of glycerin in such preparations.

According to Yates,<sup>2</sup> the hygroscopic properties of glycerin enable dyestuff pastes to be made which have excellent workability. The presence of this fluid promotes fixation and when aging conditions are on the dry side, its moisture retaining and absorbing nature comes to the fore. Moreover, increased color value is obtained from the dyes employed when glycerin is used, but this is true only up to a certain percentage. Yates employs 5% glycerin in his typical formulas.

The presence of a hygroscopic agent, such as glycerin, to assist in the screen printing of rayons has long been recognized and recently reemphasized by an authority<sup>3</sup> in this field. Russian studies<sup>4</sup> on the dyeing of fabric made of combed wool and synthetic fibers further stress the value of glycerin. In these investigations, a fabric containing cuprammonium fiber, 15%, and mestizo wool, 50%, was dyed with Sulfur Black ChF in the presence of sodium sulfide 60% (dye basis), sodium chloride 10–15%, joiner's glue 1–2% and glycerin 1–1.5% (fabric basis), at a maximum dyeing temperature of 20°C. With this procedure, the cuprammonium fiber dyes evenly throughout the fabric and the finished fabric is soft, elastic and looks normal.

Glycerin-utilizing printing and dyeing processes specify glycerin as a hygroscopic ingredient.<sup>5</sup> Glycerin has proven useful where special effects are desired. A case in point is given in a recently

patented <sup>6</sup> process for producing halftones, mat and similar effects on textiles. To achieve this, a resist is applied to the fabric with the aid of a screen or a roller. The resist, which may be underprinted or overprinted, serves to prevent the printing color from penetrating the textile or developing to the same extent as on untreated or unreserved parts. A typical resist for this purpose consists of:

	Parts by Weight
Albumin .....	50
Titanium Dioxide .....	160
Barium Chloride .....	75
Sodium Sulfate .....	50
Glycerin .....	50
Castor Oil .....	30
Gum Tragacanth (6%) .....	260
Water .....	325

The addition of a suitable discharging agent, such as a hyposulfite, to the resist produces white effects on colored backgrounds.

According to Yates,<sup>2</sup> if acetate rayon goods have been slightly delustered during dyeing or finishing by the use of too high a temperature, they can usually be improved by a treatment with an aqueous alcohol solution to which a small amount of glycerin has been added.

In sizing, as well as in weighting mixtures, glycerin, in comparatively small amounts, has a long-established place as a valuable hygroscopic agent. By its presence and because of its ability to absorb moisture from the air, glycerin prevents the starches and sizings from becoming too dry and dusting out. Moreover, glycerin also serves to counteract any drying action which is likely to occur during the actual manufacture of a fabric.<sup>2</sup>

European reinvestigations of the use of soluble starches in sizes have merely served to reaffirm the advantages of glycerin.<sup>7</sup> Thus it was found that the addition of 5% of glycerin as a softening agent was definitely beneficial; a fact long recognized by experienced textile technicians.

An interesting, typical formula for a weighting for textiles, given in the newest volume of *The Chemical Formulary*,<sup>8</sup> is pertinent and well worth mention:

	Parts by Weight
Glycerin .....	6.0
Urea .....	2.0
Potato Starch .....	2.0
Sodium Benzoate .....	0.2
Water .....	27.8

Special treatments to improve the textiles very often utilize the several advantageous qualities inherent in glycerin. A case in point is Sebrell's patented procedure for treating fabrics, more especially hose, to improve wearability by increasing their resistance to runs. According to his patents,<sup>9</sup> the breaking of stocking threads can be postponed and the life of the stocking greatly extended by coating the threads with a protective material which compacts and strengthens the fiber and permits the loops of the knitted fabric to slide smoothly over each other, thus minimizing the detrimental "sawing" action produced during walking and bending. A typical, glycerin-containing composition for this purpose is as follows:

Paraffin .....	1363	g.
Triple Pressed Stearic Acid .....	227	g.
Lanolin .....	85	g.
Soluble Oil Base .....	340	g.
Gelatin .....	283	g.
Acetanilid .....	227	g.
Glycerin .....	453	g.
Technical Dextrin .....	227	g.
Aluminum Acetate (20%) .....	3620	g.
Hexamethylene Tetramine .....	14.2	g.
Acetic Acid .....	10.0	ml.
Diastase .....	7.4	ml.
Water, to Make .....	24.6	l.

The hygroscopic and plasticizing action of glycerin, as well as its penetrating and solvent action is utilized for many types of adhesives. A patented process for making adhesives suitable for uniting plies of wood, cloth or the like, specifies that the bonding agent consists of a blood albumin-glue-hexamethylene-tetramine adhesive containing from 23 to 35% of glycerin on a dry basis.<sup>10</sup>

Glycerin-plasticized gelatin adhesives have been advocated for

laminating cloth to make poison gas resistant cloths for protecting foodstuffs and the like. In a series of annual reviews,<sup>2</sup> it has frequently been mentioned that glycerin and glycerin-containing materials afford effective barriers to the passage of poison gases, more especially mustard gas. Practical application of this fact is apparent in a recent symposium on the preservation of essential foodstuffs. In this discussion, Katz<sup>11</sup> of the Edgewood arsenal reported that the combination of gelatin with glycerin (as a plasticizer to impart flexibility) is "very resistant" to war gases. He pointed out that treatment with formaldehyde or chromates is needed to make the gelatin insoluble in water. He also observed that glue can take the place of gelatin in paulins where the glue-glycerin combination is used as the inner layer between the cloth laminations. To prevent absorption of liquid by the cloth, the use of resinous varnish coatings on the outer surfaces is advocated.

Glycerin also finds application in new types of synthetic fibers. The production of rayon offered an outstanding example of such use. The development of synthetic fibers from protein materials, such as casein from milk, further elaborated the value of glycerin. As newer proteins, e.g., soybean proteins, find use in production of synthetic fibers, glycerin likewise finds conjunct applications. An example is given in a recent patent<sup>12</sup> in which methods are described for making synthetic wool filaments, films and the like from soybean protein. According to the specifications, products made from hydrolized soybean protein are soaked in an after-treatment solution containing at least about 20% by volume of glycerin to give a desired flexibility to the treated product. After drying at a temperature not exceeding 60°C., the product is exposed to a temperature of above 100°C. for a short time (e.g., 3 minutes at 120°C.) so that the flexibility of the product is largely retained upon subsequent washing.

Synthetic resins made with glycerin, more especially the group known as alkyd resins, are used in textile treatments and the potentialities are even greater than is generally realized.<sup>13</sup> Alkyd resins are also employed in the production of gas-resistant fabrics useful in chemical warfare.<sup>14</sup>

In his recent article on *Plastic Coatings in the Post-War Era*, Cleveland<sup>14</sup> not only indicated the development and some of the potential uses of alkyd resins in the textile field, but tabulated



their general properties (along with other plastics and resins), when applied to textiles. The properties of the alkyd resins, listed below, pertain to the alkyds as a general group of resins, but it must be remembered that they can be modified in several ways to meet an almost infinite variety of needs. With this fact in mind, one may then consider the general properties of the alkyds as follows:

Solubility .....	Good
Compatibility .....	Good
Water Resistance .....	Fair
Acid Resistance .....	Fair
Alkali Resistance .....	Fair
Alcohol Resistance .....	Fair
Gasoline Resistance .....	Good
Flammability Resistance .....	Good
Heat Resistance .....	Good
Cold Resistance .....	Fair
Sunlight Resistance .....	Good
Tack Resistance .....	Fair
Flexibility .....	Good
Adhesion .....	Good
Heat-Sealing Ability .....	Poor
Abrasion Resistance .....	Fair
Color .....	Good
Odor .....	None
Price Rating .....	Low

These general properties help in part to explain the increasing use of alkyds in textile treatments and finishes. Although alkyd resins find frequent use as the sole resin employed, Cleveland is of the opinion that in fabric coatings, their use appears to be increasing as a modifier and plasticizer for other resins and various cellulose derivatives. The patent literature seems to bear out this contention, since many instances are available which illustrate the value of the alkyds in combination with other modern synthetics, not only for creating special finishes,<sup>15</sup> but also in dyeing and printing processes.<sup>16, 17</sup>

Alkyd resins have for several years constituted the major component of the varnishes used in making electrical-insulating cambric. A recent patent<sup>18</sup> describes a new method for making electrical insulating materials by treating fabric or paper with a

glycerin-phthalic anhydride-maleic anhydride resin, modified with cottonseed stearin. The finished product is claimed to be flexible, odorless, heat-resistant and age-resistant.

According to another invention,<sup>19</sup> a castor oil modified phthalic anhydride-glycerin resin can be used to treat synthetic linear polymer yarns so that sheer knit goods produced with these yarns will remain substantially free of snags and pulled threads.

Glycerin derivatives, some of them of a quite complex nature, find interesting textile applications. Thus certain polyglycerin esters have been advocated as textile assistants for softening and conditioning various textile materials,<sup>20</sup> while other derivatives have been specified as being useful in new printing and dyeing processes<sup>21,22</sup> and in special synthetic rubber coatings for fabrics.<sup>23</sup>

A valuable aid in the textile laboratory where it has long served in chemical, physical and microscopic-analytical procedures, glycerin has continued to add to its long list of uses. It is incorporated in a preparation for evaluating the effectiveness of detergents and wetting agents used in textile treatments. This preparation is a standardized soiling mixture representative of "water-bound" soil and consists of:

Lampblack .....	7 g.
Glucose Syrup .....	150 g.
Glycerin .....	150 g.
Water .....	1 gal.

This mixture, together with combinations representative of "oil-bound" soil constitute an important part of the detergent testing procedure recently outlined by a group of textile research workers.<sup>24</sup>

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## CHAPTER XVII

### TOBACCO \*

IT is not generally realized that glycerin is closely associated with the rapid rise in the use of tobacco in recent years. The fact that through the scientific control of moisture content, modern tobacco products—cigarettes, cigars and pipe mixtures—reach consumers everywhere in a fresh, firm condition that insures a mild, cool, satisfying smoke, has admittedly played a major part in the ever-growing popularity of smoking. For securing these desirable, or rather, essential characteristics, glycerin is a basic ingredient.

Because of its moisture retention ability as well as other inherent qualities, glycerin serves to maintain the necessary moisture content of tobacco without which smoking would be harsh, hot, drying and irritating. Some idea of the importance of glycerin as a hygroscopic agent may be gathered from the statement that the tobacco industry uses more than twenty million pounds of the compound annually. Furthermore, as a constituent of Cellophane and similar packaging materials for tobacco products, glycerin likewise contributes in a large measure to this basic moisture retention.

Of the hundreds of millions of pounds of tobacco grown each year, more than 50% is used to make cigarettes. In 1937, for example, American manufacturers produced almost 170 billion standard size cigarettes, an advance of about 11 billion over the previous year. During the same period, over 5 billion cigars were manufactured and over 233 million pounds of smoking tobacco were produced.<sup>1</sup> Because cigarettes dominate the industry, it is not surprising that investigators in this field have devoted much of their time and effort to the study of cigarette tobaccos and cigarette production problems. Undoubtedly, much of this information has also been of benefit to other phases of tobacco pro-

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duction and to other types of tobacco products. Such research constantly emphasizes the importance of moisture control in tobacco processing, and often serves to re-affirm the importance of glycerin as a hygroscopic agent for tobacco mixtures.

The place of a hygroscopic agent such as glycerin in cigarettes is aptly given by Bailey and Petre,<sup>2</sup> who state that "the raw materials of cigarette manufacture are leaf tobacco, a hygroscopic agent, a small amount of flavoring materials and cigarette paper."

Haag<sup>3</sup> has similarly indicated the necessity for including a "moistening" agent in the tobacco mixture to assure a satisfactory smoke. He observes that glycerin is the hygroscopic agent used almost universally, a fact acknowledged by other authorities.

A hygroscopic agent should meet certain definite requirements. It should, of course, have marked moisture-retaining ability. In addition, such a material must be combustible, non-toxic and contribute nothing deleterious to the smoke.<sup>4</sup> Glycerin meets these requisites fully.

Glycerin is outstanding among modern materials for its ability to attract and retain moisture. Brown,<sup>5</sup> in a recent review of the properties of glycerin, emphasizes this hygroscopic action and states that commercial glycerin on exposure to air will absorb as high as 40% moisture over a period of a month. He writes that this attraction for water is due to the formation of a hydrate.

Glycerin will continue to attract moisture, even under comparatively arid conditions. It does not evaporate even under extreme climatic variations because of its high boiling point (290°C., when pure). This is an important consideration when it is remembered that American tobacco products are shipped all over the world, to say nothing of a varied-climate nation such as the United States.

Glycerin has a sweet warm taste in the mouth. The absolute wholesomeness and purity of the fluid have been proven not only by decades of use, but also by thoroughgoing laboratory investigations on animals and humans.<sup>6, 7</sup>

From the smoking viewpoint, the observation of Ballenger and Johnson<sup>8</sup> is most pertinent: "Glycerin is not irritating to the respiratory mucosa, as attested by its frequent use in medications for the nose and throat." This is an important consideration, since it is now known that a small proportion of unchanged hygro-

scopic material in tobacco mixtures comes over in the main smoke screen.<sup>9</sup>

Properties that make glycerin so valuable in the tobacco industry have been well summed up by Levey,<sup>10</sup> who, in speaking of glycerin consumption, reports: "The tobacco industry is one of these large volume consumers. Glycerol (glycerin) is added as a softening agent and to facilitate the maintenance of a given moisture content, as well as to give sweetness and improved flavor to the tobacco."

It might well be said that tobacco processing, no matter what the eventual type of product, is practically one continuous moisture control problem—a cycle of drying and humidifying.

Almost twenty years ago, Chesley,<sup>11</sup> one of the first modern tobacco technologists, observed: "Few materials are so affected by changes in humidity as tobacco. The writer has found that if conditions are favorable, tobacco will take on moisture until it contains as much as thirty per cent." As far as the manufacturer is concerned, moisture control begins immediately after purchase of the leaves.

In the casing mixture, especially for cigarettes, glycerin is an important factor. Often the solution consists only of glycerin and water. The glycerin content of this casing solution is essential in assuring that the tobacco, in its final form, will have and maintain its proper moisture content and that the cigarettes will be fresh and palatable no matter when or where the package is opened. Glycerin keeps indefinitely and does not turn rancid.

After the flavoring and before being sent to the cigarette-making machines, the moisture content of the shredded tobaccos are again adjusted, this time to a final value of very close to 12%, as less moisture has been found to yield a harsh, dry smoke and more might induce molding. But in the presence of about 3% of glycerin as the hygroscopic agent, the cigarette filler at this moisture content may be handled without excess crumbling since it is as pliable as untreated leaf at 15% moisture. This glycerin addition also serves to equalize the variations in the average relative humidity encountered in the various parts of this country. The full plumpness of cigarettes, indicative of freshness, may, therefore, be attributed, to a large extent at least, to the glycerin present in them.

Glycerin is not a normal ingredient of cigarette papers. However, a special paper-impregnating material, designed to prevent smoldering of discarded cigarettes, should be of interest. This special cigarette wrapper, according to the patent specifications,<sup>12</sup> can be made by impregnating a zone of the paper with a mixture containing waterglass, glycerin, starch and talc.

In recent years, much attention has been given to the constituents of tobacco smoke,<sup>13, 14</sup> which after all is an end of most tobacco, the obvious exceptions being chewing tobaccos and snuff. A good deal has been learned with regard to the fate and effects of the hygroscopic agent used.

Actually, the amount of unchanged hygroscopic agent, such as glycerin, that makes its way into the mouth and respiratory passages by way of the "main stream" smoke, is very small. But small as it is, the importance of using a safe, non-toxic material is self-evident. Forbes and Haag<sup>9</sup> have determined that from 7 to 8% of the total semi-solid constituents consists of unchanged hygroscopic material. Of this, only 22% is transferred to the main smoke stream, the rest passes into the side smoke stream or is deposited in the butt.

The following table (based on a 35 ml. puff of 2 seconds duration, once a minute, the average cigarette lasting ten minutes), taken from a recent report,<sup>3</sup> gives a clearer indication of the relative proportion of hygroscopic agent with regard to the other constituents of the main smoke stream from a cigarette:

Carbon Dioxide .....	35.00 ml./cigarette
Carbon Monoxide .....	10.00 ml./cigarette
Moisture .....	15.00 mg./cigarette
Dry Solids .....	40.00 mg./cigarette
Nicotine .....	3.00 mg./cigarette
Other Volatile Bases .....	0.25 mg./cigarette
Formic Acid .....	0.50 mg./cigarette
Other Volatile Acids .....	1.70 mg./cigarette
Benzoic Acid .....	Trace
Phenols .....	0.15 mg./cigarette
Aldehydes .....	1.25 mg./cigarette
Hygroscopic Agent .....	3.00 mg./cigarette

Other laboratory and clinical tests on cigarettes have shown that no hygroscopic agent for tobacco use is superior to glycerin

with regard to safety, lack of toxicity and efficiency.<sup>8, 15, 16, 17, 18</sup>

A check of the patent literature indicates that glycerin enters extensively into various processes for improving tobaccos for all purposes. One such composition<sup>19</sup> for improving tobacco is specified to contain:

	Parts by Weight
Invert Sugar or Honey .....	100- 500
Potassium Salt .....	3- 6
Zinc Sulfate .....	2- 6
Sodium Chloride .....	4- 8
Glycerin .....	30- 60
Saffron .....	1- 2
Water .....	1000

In another instance,<sup>20</sup> a process for irradiation and other treatment of tobacco, the tobacco is dampened with water to which a "sauce" containing coumarin and the like has been added. Glycerin is also a recommended ingredient of this dampening solution to give it clarity. The mixture is applied to the tobacco prior to the irradiation.

In a more recent patent,<sup>21</sup> a glycerin derivative is utilized. Here it is stated that a cigarette tobacco, containing little nicotine and producing a white ash, may be obtained by treating tobacco with a solution containing calcium nitrate, magnesium nitrate and a glycerin ester of phosphoric acid. An aqueous solution, containing 3% of the glycerin ester and 0.2% of each of the nitrates, is a preferred combination for tobacco treatment.

An interesting glycerin-containing mixture has been recommended as a flavoring combination for salvaging scrap tobacco to be used for smoking.<sup>22</sup> Following formula provides enough solution to treat one hundred pounds of the scrap tobacco:

Glycerin .....	1 lb.
White Sugar .....	1 lb.
Maple Sugar .....	1½ lb.
Honey .....	1½ lb.
Water .....	4 to 6 lb.

Amount of water used will vary with the condition of the tobacco.

In another, more indirect, but perhaps equally important way, glycerin further works to conserve the essential moisture content,



and thus the freshness of tobacco products. Glycerin performs this function as an ingredient of cellulosic transparent wrapping materials, such as Cellophane. Here glycerin serves to maintain the pliability of these modern packaging materials.<sup>23</sup>

Even though a hygroscopic agent, such as glycerin, greatly assists in retaining moisture, a moisture-impervious wrapper is also essential. In the old days, much of the water content was lost, along with most of the aromatic flavoring materials.<sup>2</sup> Glassine papers were the first step toward remedying this situation. Glycerin is a frequent constituent of such papers. Cellophane, in which glycerin is the softening or hygroscopic base, was a marked improvement. It has been estimated that such wrappings have cut moisture losses or gains to a fourth the rate of unwrapped packages.<sup>4</sup>

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## CHAPTER XVIII

### GLASS

GLYCERIN AND its derivatives play a versatile role among the materials which are contributing to make modern glass useful and valuable. This unique fluid finds use, not only in the manufacture of the newer materials, such as "safety" glass, but is also a valued ingredient of such standard substances as etching compounds, anti-fog and anti-mist products, glass polishes, glass-marking inks and the like.

Among the most widely utilized of the glycerin derivatives are the synthetic glycerin phthalate resins, referred to as alkyd or glyptal resins. Alone, or in combination with other materials these glycerin-containing resins have found important uses in the manufacture of laminated or safety glass. The industrial literature is replete with references to such uses for these resins. In the past unmodified alkyd resins were employed<sup>1</sup> and showed strong adhesive powers and resistance to moisture, but had the disadvantage of eventually becoming brittle due to polymerization. This disadvantage has been overcome, and other desirable properties imparted to these resins by the use of oils or fatty acids as modifying agents. A typical, patented,<sup>2</sup> alkyd resin of this sort may consist of:

	Parts by Weight
Glycerin .....	94
Phthalic Anhydride .....	148
Castor Oil Fatty Acids .....	40
Corn Oil .....	100

Quite frequently sheets of flexible alkyd resin are used for uniting two sheets of glass,<sup>3</sup> but more often these glycerin-containing products are employed as bonding agents for uniting glass sheets with intervening transparent materials, such as cellulose ester compositions.<sup>4</sup>

A resin-like product for laminating glass can be made by heating together glycerin, and a protein, such as casein; and adding phthalic anhydride to the reaction product with further heating.<sup>5</sup> An adhesive for similar uses may be prepared by heating together casein, glycerin and sodium hydroxide.<sup>6</sup> Coagulated calcium alginate films are washed free of soluble salts with a glycerin solution, prior to use in making non-shattering glass.<sup>7</sup> Glycerin likewise enters into methods for uniting celluloid or the like to glass in making compound glass.<sup>8</sup> Newer laminating materials, such as polyvinyl alcohol, similarly employ glycerin or glycerin aldehydes which serve to give improved adhesive properties.<sup>9</sup>

When gelatin is employed as a laminating agent for making safety glass, glycerin is a standard adjunct material. In one case,<sup>10</sup> a glycerin solution containing 15–25% of acetic acid is coated on the glass sheets prior to their union with gelatin by pressure. Pegler, in a series of patents, advocates the employment of glycerin as a plasticizing agent for gelatin sheets used for making non-shattering safety glass.<sup>11</sup> Others similarly advocate glycerin as a plasticizer for gelatin glass-laminating films.<sup>12</sup>

Glycerin derivatives, particularly glycerin triacetate or triacetin, which is widely used as a camphor substitute, are employed as plasticizing agents for transparent glass-laminating agents, such as cellulose acetate,<sup>13</sup> cellulose nitrate<sup>14</sup> and similar cellulosic derivatives.<sup>15</sup> Glycerin diacetate or triacetate is also recommended as a plasticizing agent for polyvinyl esters similarly employed in compound glass manufacture.<sup>16</sup> Glycerin formal has likewise been advocated as a plasticizer for similar polyvinyl resins used in place of glass.<sup>17</sup>

For securing adhesion between glass and metals, glycerin litharge cements, which may readily be prepared just prior to use by mixing glycerin with litharge to form a paste of the desired consistency, find advantageous usage. These cements, the composition of which may be varied by the addition of various other substances, set rapidly to an almost incredible hardness and strength. Very recently, Ziener,<sup>18</sup> a European authority, pointing out that glass is being used more and more to replace metals, advocated the use of a glycerin-litharge cement to join metal to glass. This writer, who also discusses the cement raw materials, their mixing and application, recommends this cement on the basis

that it is heat proof, up to  $260^{\circ}\text{C}$ ., withstands the action of acids, bases, and many organic liquids as well as being gas-tight at pressures below six to eight atmospheres. He also mentions the fact, well-known to everyone familiar with the various glycerin-litharge cements, that these products can be used to join many other materials.

Glass-etching processes, whether physical or chemical, frequently make use of one or more properties of glycerin. Stout<sup>19</sup> recommends glycerin as a glass grinding fluid, inasmuch as it has sufficient body to carry the emery or other abrasive, and furthermore, being water-soluble, the ground-glass surfaces are easily cleaned. It may also be mentioned that glycerin is used for rendering ground glass temporarily transparent. Glue-glycerin sheet compositions are used as stencils in sand-etching glass. The sheet is applied to the glass and the design is then cut into the glue sheet, which is strong and resilient enough to withstand the sandblasting action, but the particles readily etch the glass in the desired design or inscription.<sup>20</sup> Glass-etching fluids, in which a fluoride is the active chemical ingredient, use glycerin as a constituent. To prepare one type of glass-etching paste, ammonium bifluoride is mixed with just enough water to dissolve the crystals. With this, a quantity of glycerin equal to half the volume of the liquid is mixed, and then calcium sulfate added until the mixture thickens to a thin paste. A similar glass-etching paste consists of:

	Parts by Weight
Glycerin .....	4
Gum Karaya .....	2

These are rubbed together well and the following ingredient is worked in:

	Parts by Weight
Ammonium Fluoride (Concentrated Solution) .....	94

It is hardly necessary to point out that all of these fluoride-containing products are dangerous and must be used and handled with care, in a well-ventilated room. They should be stored in hard rubber or lead bottles.

A glass marking "ink," which depends on a fluoride etching action is made as follows:

	Parts by Weight
Hot Water .....	12
Ammonium Bifluoride .....	15
Oxalic Acid .....	8
Ammonium Sulfate .....	10
Glycerin .....	40
Barium Sulfate .....	15

The viscosity may be adjusted by adding water. An ordinary steel pen may be used for writing on the glass which should be slightly warmed. The ink is allowed to act for about two minutes, then it is washed off with hot water and dried. The pen must also be washed. The addition of about 2% sodium fluoride speeds up the action and improves the ink.

Another glass-marking ink, green in color, which is applicable to thin, blown glassware, but not for heavy cast glass objects, is made by mixing equal parts of chromic oxide with powdered lead borate. These are stirred into a solution made up of equal parts of alcohol, water and glycerin; the amount of liquid used depending on the consistency desired. The ink is applied with a pen and allowed to dry. When dry, it is fixed by slowly warming the glass in a yellow gas flame, then it is heated to red-hot in the blue flame. The glass is then slowly cooled, using the yellow flame to lower the temperature and so prevent unequal stresses and strains in the glass.

According to a patented process<sup>21</sup> polished glass articles, such as lenses, mirrors, and the like, may be marked for identification by means of a soluble glycerin phthalate paint. Articles so marked are then heated until the paint is polymerized to the desired extent. Glycerin is also sometimes used in glass-lettering paints to prevent excessive drying, cracking or chipping. For the same reason, glycerin is added to colored water glass or gelatin solutions used for tinting electric-light bulbs, globes and similar glass objects.

Glycerin solutions are of marked value in protecting glass windows during spray painting. Studies made by a large mid-western railway company proved that a solution of glycerin and whiting was far superior, both from the angle of cost and efficiency, than any other material tried. This solution was found to give uniform action under all weather conditions and afforded a notable decrease in the time and effort required to clean the train windows. Breakage, too, was markedly less. A glass-masking coating for use while painting automobiles may be made with:

	Parts by Weight
Kaolin .....	5.0
Glycerin .....	1.5
Butyl Alcohol .....	0.25

This is applied to the automobile glass with a brush and allowed to dry. After the spray painting, the mask may be easily removed with a cloth, a putty knife or by washing with water, leaving the glass free of paint.

Glycerin-containing materials are also used sometimes to protect mirrors and similar metal-coated glass reflectors. In one process,<sup>22</sup> a layer of silver on glass is coated with copper and then with an overlaying, protective coating composed mainly of a glycerin phthalate resin and containing a metallic pigment, such as powdered aluminum.

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## CHAPTER XIX

### AGRICULTURE

PROBABLY NO other product of its kind lends itself to such a variety of uses in modern farming practice as glycerin. Practically every farmer knows this substance to some extent. Comparatively few, however, appreciate the wider possibilities which glycerin offers and which may be advantageously utilized on the farm proper, in and about the farm house and other farm buildings, in the maintenance of farm equipment, and on the livestock.

Glycerin not only finds helpful application in such new phases of agriculture as seed germination treatments but also in such standard items as sprays of all types, insecticides, pest destroyers, and many forms of animal preparations. Since many of these products may be made by the farmer himself from readily available materials, a number of suggested formulas will be included in this chapter.

One of the newest applications of glycerin in solving farm problems is its use in the treatment of seeds and seedlings. In Europe, where self-sufficiency has become a major issue, studies have shown that the germination of oats is stimulated by the use of dilute solutions of glycerin, the phases being accelerated by two to nine days and sometimes increasing the amount of dry substance. Other winter cereals and some spring cereals were also found to be stimulated by similar treatment. It was found that oil-bearing seeds of such plants as flax, hemp, and mustard germinate in more concentrated glycerin solutions just as well and as rapidly as in water. This is an important factor, because recent preliminary American experimental studies have shown that the stimulation of plants by small amounts of glycerin may have important uses during transplantation periods.

Glycerin has long been used in connection with the treatment of plants and trees. For example, Chester's formaldehyde-glycerin



wash is a standard preparation for treating pear-tree canker. It consists of:

	Parts by Weight
Solution of Formaldehyde .....	1
Glycerin .....	2
Water .....	17

Quite recently, tests with various combinations for coating tree wounds to overcome infection (by *Polystictus versicolor*) proved the superiority of a glycerin-containing preparation. After trying Bordeaux paste, creosote, linseed oil paint, coal tar, grafting wax, heavy petroleum jelly, and a bitumen emulsion, a glycerin mercury salt combination, applied twice at 21 day intervals, was found to control the worst cases of tree infection. This mixture is prepared by heating together 3 quarts of glycerin and 1 quart of water to 170°F., and adding  $\frac{1}{4}$  oz. of mercuric cyanide and  $\frac{1}{4}$  oz. of mercuric chloride.

Because of its unusual solvent powers, glycerin is frequently employed in making insecticides and insecticidal sprays. Likewise glycerin is a good dispersing agent and has a fairly high penetration value. Since it is viscous, it is sometimes used to give body to such products. One typical, patented insecticidal emulsion, in which lead arsenate is the killing agent, glycerin is specified as one of the four ingredients. This emulsion is sufficiently stable for spraying upon dilution with up to about 300 times its volume of water. Glycerin is sometimes included as a hygroscopic agent in special Bordeaux mixtures, to be diluted for spraying. Chemical reaction products of glycerin are widely utilized as emulsifying and dispersing agents for making insecticidal sprays.

Many insect-destroying preparations, not of the spray type, employ glycerin. Mercuric chloride is extensively used for destroying bugs. Typical is the following:

	Parts by Weight
Mercuric Chloride .....	4
Ammonium Chloride .....	4
Water .....	80

The ingredients are dissolved and the following mixed in:

	Parts by Weight
Glycerin .....	4
Wood Naphtha .....	80

This is to be brushed over the parts where the pests live, and it is a good plan to add about half a pint of this solution to each bucketful of whitewash used for cleaning the walls and ceiling. Particular attention should be given to cracks in the woodwork where the insects crawl and hide.

Getting rid of earwigs is always a problem and requires close cooperation among all the farmers in the district where the pests are found. The use of natural enemies of this insect is being studied, but the work with poison baits is of very considerable interest. Arsenic is the best poison to use, but the large number of drawbacks to the use of this chemical, makes the employment of sodium fluoride more feasible. Sodium fluoride, though to a lesser degree, is poisonous too, and must be used with caution. It has been shown that a bran bait containing this substance was the best, from the viewpoint of effectiveness and economy. One of the most highly recommended formulas is the following glycerin-containing preparation.

	Parts by Weight
Sodium Fluoride .....	1
Molasses .....	5
Glycerin .....	5
Water .....	5
Ground Oat Hulls, about .....	16

First the sodium fluoride and then the molasses are dissolved in the water. The bran (or oat hulls) is added last.

This preparation does not dry up quickly and is particularly suited for late summer use. The bait should be scattered over the ground and small quantities placed in the crotches of trees or at intervals along fences and walls.

Fly exterminators and sprays, so necessary around barns and such, frequently include glycerin. One old-fashioned and still highly effective method of keeping away flies consists of exposing a shallow dish or pan of dilute formaldehyde where these insects are apt to gather. The following solution has been found especially effective:

Solution of Formaldehyde .....	6 drams
Glycerin .....	1 oz.
Water .....	30 oz.

Similarly, formaldehyde-glycerin combinations are used in fly-sprays, of which this one is typical:

	Parts by Weight
Solution of Formaldehyde .....	3
Glycerin .....	5
Water, to Make .....	100

A more modern fly-spray preparation can, however, be made from:

	Parts by Weight
Tincture (Alcoholic Extract of Pyrethrum Flowers) .....	50
Soft Soap .....	18
Glycerin .....	24
Carbon Tetrachloride .....	3

To use this solution, 5 parts of it are diluted with 15 parts of water.

Nicotine preparations for fumigation of greenhouses are much used today and are especially effective against thrips. These liquid fumigants are used at the rate of 1 oz. to every 1000 cubic foot of space. The preparation should be evaporated over small lamps or stoves, preferably diluted with two parts of water, at night, in the moist atmosphere of the closed greenhouse. A typical vaporizing and fumigating insecticide consists of:

	Parts by Weight
Nicotine .....	39
Camphor .....	23
Alcohol .....	28
Glycerin .....	10

Poison baits for rats and field mice also may utilize the action of glycerin to heighten their effectiveness. Thus, glycerin may be used in combination with such pest-poisons as barium sulfate, thallium sulfate and phosphorus. A typical field mouse poison is given in this phosphorus paste:

	Parts by Weight
Gelatin .....	25
Boiling Water .....	500

The ingredients are dissolved and the following mixed in:

	Parts by Weight
Glycerin .....	100
Phosphorus .....	20
Flour .....	500

Preparations for preventing, clearing, and treating live-stock insect infestations and diseases traceable to them are an important part of the farmer's equipment. Such products are of great economic importance since these insect diseases cause high annual losses in dead or injured animals that must be destroyed as unfit or unsafe. Sheep, because of their wool and their meat, comprise a large part of the nation's agricultural wealth. Their thick wool coating is, however, a favorite feeding and breeding place for ticks, maggots and the like. About twenty years ago, after other methods had proved ineffective, government experts turned to the use of sheep dips. Early products were improved rapidly and today are highly efficient. One easily prepared carbolic and glycerin dip, which has been used with good results is the following:

	lb.
Common Size .....	1
Soft Soap .....	1
Crude Glycerin .....	1
Crude Carbolic Acid .....	1

The size and soap are melted together and the other ingredients added and mixed well. This quantity is used to make 30 gallons of sheep dip.

Very recently, Dr. Mason presented a new sheep dip formula, a compound of glycerin and arsenious oxide, which can be made by simply mixing and heating until a clear syrupy liquid is obtained. The ingredients

	Parts by Weight
Arsenious Oxide .....	45
Water .....	12
Glycerin (Anhydrous) .....	43

are heated at 150°C. If commercial glycerin, containing varying amounts of water, is used, the temperature should be reduced to 100°C. and heated for a longer period. Although this product may be used in combination with other dips, it is claimed that,

used alone, it is as effective as the now popular arsenic, sulfur, and phenolic mixtures. Also it is said that its potency is not lessened by hard water.

A Canadian Department of Agriculture handbook on animal insects and parasites points out that, "A number of common flies, normally breeding in carrion, will sometimes 'strike' living animals if suitable conditions occur and the maggot infestation, known as myiasis, may result in sufficiently severe injury to cause death." All precautions must, of course, be taken to prevent the breeding of blow flies and the like, but when animals have become maggot-infested, promptness is essential. In the case of sheep, it is advised that the wool be removed from around infested area. If the maggots have penetrated deeply, an application of glycerin will bring them to the surface, where they may be killed with benzol (benzine). Gasoline, carbon-tetrachloride or chloroform are also fairly efficient and may replace the benzine which, however, is best. A dressing of oil of pine tar over the wound will help healing and prevent further fly-blow.

As glycerin enters so extensively into the treatment of human ailments, it is to be expected that it would find similar uses in veterinary medicine. Ear mange, for example, is not difficult to control in dogs, cats, and rabbits, if a preparation consisting of 1% cresol, 1% carbolic acid or creosote added to glycerin is used. The inside of the ear is swabbed with a cotton swab held with forceps and moistened with this glycerin solution. Care must be taken to avoid injury to the animal's eardrums. The matter and other detritus in the ear is then carefully cleaned out with a swab and the solution again applied. After seven days, this treatment should be again repeated to destroy any mites that may have been present in the egg stage during the first treatment.

For ear trouble in dogs, a preparation very similar to that used for humans may be used to relieve the irritation and pain. This consists of:

Boric Acid .....	1 dr.
Glycerin .....	1 oz.
Phenol .....	16 gr.

The boric acid is dissolved in the glycerin with gentle heat and then the phenol added. This may be applied to the cracks in the ear flaps or, if necessary, warmed and introduced into the inner ear.

The tender feet of dogs, worn and cut on crusted snow or hard ground, may be treated with an old standard mixture of equal parts of glycerin and tannic acid. This will stop the oozing of fluid and will help to dry up the raw flesh to some extent.

Glycerin is also frequently employed in nutritional cattle feeds, especially those made with cod liver oil emulsions or the like. That glycerin may sometimes be employed in the manufacture of special fertilizer mixtures was brought out in a recent British patented process where this fluid was made an integral part of the formula. The discovery of the nutritional and moisture-retaining value of glycerin in the soil may point the way to its inclusion in many such preparations of the future.

## COSMETICS

MOST COSMETIC technicians are familiar with the properties of glycerin which make it so valuable in beauty preparations and related products. However, even at the risk of appearing repetitious, it may be worth while to review briefly the uses which make glycerin helpful in so many ways. These, as presented by Merrill,<sup>1</sup> at the 1943 T.G.A. meeting, are as follows: (a) as a humectant; (b) as a vehicle; (c) as a solvent; (d) as a sweetening agent; (e) as an emollient; (f) as a reactive material; (g) as a lubricant; (h) as a softening agent; (i) as a penetrant; and (j) as an anti-freezing agent. To this might well have been added the fact that glycerin is completely free of toxic effects.

This list offers a good explanation why no satisfactory substitute has been developed. Although some substances or combinations of substances have duplicated individual properties of glycerin, the over-all characteristics of this valuable material cannot be reproduced. This is a fact established, not only by authoritative American research,<sup>1, 2, 3</sup> but also by extensive British investigations.<sup>4</sup> Nor can one overlook the fact that the government has found it necessary to issue a warning concerning the use of certain toxic substances suggested as substitutes for glycerin.<sup>5</sup>

As new materials are developed for or adopted to cosmetic use, glycerin has found concurrent and valuable use to improve or impart certain desirable characteristics.

In 1938, when sodium alginate, a derivative of seaweed, was being advocated for use as a cosmetic raw material, it became clearly evident that glycerin was a valuable conjunct aid in the formulation of wave sets, dentrifices, hand lotions and the like. Indeed, according to Bergy,<sup>6</sup> glycerin is useful in the preparation of the sodium alginate solutions. He advises to add the algin in a thin stream to either hot or cold water with constant stirring. To avoid clotting it is advisable to wet the sodium alginate with glycerin before adding to the water.

An illustration of the use of glycerin in connection with this material is offered in Jannaway's <sup>7</sup> formula for a greaseless hair pomade:

	Parts by Weight
A. Sodium Alginate .....	2.5
Distilled Water .....	100.0
Perfume .....	1.0
Glycerin .....	5.0
Parahydroxybenzoic Acid Ester .....	0.25
	Parts by Weight
B. Calcium Citrate .....	0.2
Distilled Water .....	90.0

Solution A. is prepared by dissolving the alginate and preservative in the water, to which is added the perfume and glycerin. In part B., the citrate is stirred with 90 parts of water and then mixed with solution A. The pomade is allowed to stand for two hours to permit complete thickening.

Glycerin is also used in formulas utilizing methyl cellulose. Methyl cellulose is neutral; resistant to acids, alkalies and bacteria; it is innocuous, and forms mucilages which may take the place of the vegetable gum mucilages. It may be used to prepare emulsions of the o/w variety.<sup>8</sup> Glycerin has found extensive use with these materials in the formulation of dentifrices, depilatories, dermal creams, emollient creams, cleansing creams and similar preparations.<sup>9, 10, 11</sup> A typical glycerin-utilizing matt skin cream base on methyl cellulose, given by Vallence,<sup>12</sup> is as follows:

	Parts by Weight
Triple Pressed Stearic Acid .....	9.5
Cetyl Alcohol .....	0.5
Mineral Oil .....	2.0
Groundnut Oil .....	2.5
Methyl Cellulose Solutions (4%) .....	25.0
Glycerin .....	5.0
Borax .....	0.5
Ammonia (0.97) .....	1.0
Perfume Oil .....	0.5
Distilled Water .....	53.5

Lanette Wax SX, introduced as a cosmetic by British workers, is a more recent and very interesting material frequently used



together with glycerin in the formulation of cold creams of the matt cream type, day creams, night creams, baby creams, stocking simulating creams, etc.<sup>8, 13, 14</sup> Lanette Wax SX, as now standardized, is a partially sulfated or phosphated mixture of cetyl and steary alcohols. It contains a good base and also an emulsifying agent producing neutral and stable emulsions. Typical of the use of glycerin in conjunction with this whitish wax is the following simple day cream formula suggested by Allen:<sup>13</sup>

	Parts by Weight
Lanette Wax SX .....	15
Glycerin .....	7
Water .....	78

This cream can form the base for the now so popular stocking-simulating creams. The following formula has been suggested as a basis for experiment:<sup>13</sup>

	Parts by Weight
Lanette Wax SX Vanishing Cream (Day) .	62
Gum Solution (Tragacanth, Karaya, etc.) ..	2
Titanium Dioxide .....	1
Colloidal China Clay .....	3
Face Powder Base (Sun Tan, etc.) .....	12
Glycerin .....	5
Water .....	15

Pectin, now officially a pharmaceutical material, was long recognized as having many potentialities in the cosmetic field for the preparation of hair setting lotions, hair creams, non-fatty face creams, skin lotions, dentifrices.<sup>12, 15, 16</sup> In most of its uses, both pharmaceutical and cosmetic, glycerin is a standard adjunct to pectin. Illustrative is Goodman's<sup>17</sup> formula for a pectin hair pomade:

	Parts by Weight
Pectin .....	1
Glycerin .....	4
Water, to Make .....	100

Bentonite, the colloidal clay finds increasing use in cosmetic manufacture for the production of beauty masks and packs, creams, manicure preparations, liquid powders, dentifrices, and

other cosmetic products.<sup>12, 18, 19, 20, 21</sup> Glycerin finds many uses in conjunction with bentonite, e.g., in Glenn's<sup>22</sup> formula for a liquid powder:

	Parts by Weight
Colloidal Kaolin .....	7
Titanium Dioxide .....	5
Bentonite .....	5
Water .....	78
Glycerin .....	5
Pigment or Color .....	Sufficient

Products based upon inert gelatinous alumina and similar compounds offer many interesting possibilities in the field of cosmetics but do not seem to have been exploited to any great extent in the United States. In England, according to Vallence,<sup>12</sup> gelatinous alumina has been used as bacteria-resistant, non-frothing, emulsifying agent. He considers it very promising as a base for hair fixatives and face packs in paste form. A product that has been used in the production of calamine creams (acne cream or as a foundation for women with very greasy skins), is made from:

	Parts by Weight
Sifted Calamine .....	8
Colloidal Kaolin .....	2
Zinc Oxide .....	10
Groundnut Oil .....	25
Glycerin .....	10
Inert Gelatinous Alumina .....	35
Distilled Water .....	80-100

The emulsifier is dispersed in the water, followed by the glycerin and oil. The emulsion is heated gently, mixed and homogenized. Then the mixed powders are milled in.

Alumina hydrogel forms the basis of a patented process<sup>23</sup> for making ointment and cosmetic bases, especially astringent deodorant and anti-perspirant preparations. Claimed to provide a non-irritating, non-hardening unguent-like material that may readily be adjusted to the required pH, specific directions are given for forming a special aluminum hydroxide precipitate and mixing this product with a hygroscopic agent, such as glycerin. This

addition serves both as a plasticizing agent and as a solvent for the medicinal, coloring and perfuming materials. An example of a typical astringent and deodorant as given in the patent, is as follows:

	Parts by Weight
Alumina Hydrogel .....	100
Glycerin .....	25- 60
Benzoic Acid .....	1
Zinc Oxide .....	1
Perfume and Color .....	Sufficient

As advances are made in the field of cosmetics, glycerin keeps pace with progress. This is quite apparent, for example, in the formulation of cosmetic stockings. An inevitable development because of the comfort and freedom offered by these stocking-simulating preparations, the war-born shortage of silk and nylon for hosiery has greatly stimulated the popularity of this new type of product. Cosmetic authorities,<sup>24, 25, 26</sup> agree that glycerin in these products definitely helps, its presence affording not only an emollient effect and slight luster, but also imparting requisite flexibility to the film. Many formulas for cosmetic stockings in liquid, powder, lotion, and cream forms that take advantage of these qualities are available in both the technical and patent literature. Redgrove,<sup>26</sup> for example, after the study of a rather complex commercial preparation, evolved the following satisfactory formula:

	%
Liquid Paraffin .....	1
Glyceryl Monostearate (Containing a Trace of Soap) .....	6
Distilled Water .....	48
Glycerin .....	15
Titanium Dioxide and Earth Pigments ....	21
Talc .....	9
Perfume .....	Sufficient

Kalish's<sup>24</sup> extensive study of the subject likewise indicates the role of glycerin in these products. One of his representative compositions is as follows:

	Parts by Weight
Precipitated Chalk .....	10.0
Talc .....	5.0
Titanium Dioxide .....	3.0
Bentonite .....	2.0
Alcohol .....	8.0
Glycerin .....	3.0
Wetting Agent .....	0.5
Methyl Cellulose .....	0.5
Water .....	68.0
Dye and Pigment .....	Sufficient

The patent literature is also represented. In his discussion on cosmetic stockings, deNavarre<sup>27</sup> cites a British patent (433,142) in which the following formula is given:

	Parts by Weight
Zinc Stearate .....	3.8
Undecylic Acid .....	0.2
Titanium Dioxide .....	8.0
Talc .....	10.5
Glycerin .....	6.0
Distilled Water and Perfume, to Make ...	100.0

In deNavarre's opinion, the covering power of this product is too high, but this can readily be remedied. The use of the undecylic acid and zinc stearate affords the desired waterproofing effect.

Newer make-up foundations and powder bases continue to utilize the advantageous properties of glycerin. Thus, a foundation for make-up, based upon glyceryl monostearate (itself a glycerin derivative) contains:<sup>28</sup>

	Parts by Weight
Glyceryl Monostearate .....	20.0
Spermaceti .....	5.0
Glycerin .....	5.0
Pigment .....	3.0
Perfume .....	0.5
Preservative .....	0.1
Water .....	66.4

Hair preparations of many types use glycerin as a standard component. Thus, Vallence,<sup>29</sup> in a consideration of post-war hair

preparations, gave the following typical formula as an example of a non-greasy hair cream or brilliantine:

	Parts by Weight
Gum Tragacanth .....	1.0
Tincture of Benzoin .....	2.0
Castor Oil .....	1.5
Glycerin .....	3.5
Mineral Oil .....	6.0
Industrial Spirit .....	4.0
Perfume .....	0.4
Formaldehyde .....	0.1
Water .....	81.5

Considerable research has gone into improved shaving preparations of many types during recent years into which glycerin also enters. A British patent<sup>30</sup> describes a method for making a depilatory-shave product which in its final form is a stone-like block containing depilatory or hair softening ingredients.

This product is rubbed over the moistened beard not producing a lather, but facilitating the shaving off the beard with a razor in the ordinary way without the use of a shaving soap or a similar compound. Although glycerin is not absolutely essential, the patent states that its inclusion is desirable because it produces an agreeable emollient effect on the skin.

Electric shaving devices are presumed to be sufficient in themselves to give a satisfactory shave. Nonetheless, it has very often been found that for persons with a tender skin, a tough beard or both, an after-shave lotion is quite desirable, especially during the early breaking-in stage. To meet this requirement Hooper<sup>31</sup> has suggested the following electric razor after-shave lotion:

	fl. oz.
Liquid Extract of Witch Hazel .....	2
Glycerin .....	1
Industrial Spirit .....	$\frac{1}{2}$
Rose Water .....	4

If required, two grains of menthol may be added to this formula.

Cosmetic cleansing pads, which started off with such promise a few years ago, are but little mentioned today. Just for the record, it is interesting to note that glycerin has been a regular ingredient of the fluids used to impregnate the cloth pads. A

typical clear lotion for such impregnating fluids, given by Maiki,<sup>32</sup> is as follows:

	%
Glycerin .....	5
Alcohol .....	5
Detergent .....	1
Water .....	89
Preservative and Perfume .....	Sufficient

Milky emulsified lotions for this purpose also contained glycerin as an essential ingredient.<sup>32, 33, 34</sup>

Growing awareness of the importance of pH in preparations for use on the skin has led to the development of acid creams and other cosmetic preparations. That glycerin plays an important role in such preparations is evident from the pioneering work of both Harry<sup>35</sup> and Jannaway.<sup>36</sup> A typical acid cream, as presented by the latter investigator, is as follows:

	Parts by Weight
Pure Glycol Distearate .....	14.0
Mineral Oil .....	3.0
White Beeswax .....	2.0
Ceresin .....	1.0
Lanolin .....	1.0
Sodium Lauryl Sulfate .....	1.0
Citrus Pectin .....	0.5
Perfume .....	0.5
Citric Acid .....	2.0
Glycerin .....	6.0
Distilled Water .....	69.0

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## CHAPTER XXI

### BEVERAGES

PROMINENT is the use of glycerin both in wine and liquors and in carbonated beverages and other soft drinks, where it is an ingredient not only of the flavoring extracts and essences but also of the syrups, coloring agents and foaming preparations.

Tables, with the associated information for making glycerin-containing artificial fruit-essences, published as far back as 1866, are still valuable today.<sup>1</sup> Since that time, the steadily increasing use of this pure wholesome fluid for this and similar soft drinks has continued to grow so that at present enormous quantities of it are consumed annually by those who purvey to the national thirst.<sup>2</sup>

The natural sweetness of glycerin is a further desirable characteristic in favor of its use in thirst-quenchers. Tests performed at the University of Maryland, have shown that glycerin rates even higher than sucrose in sweetness. Taste tests performed on a group of standardized individuals gave glycerin a rating of 108 as compared with that of sugar at 100.<sup>3</sup> Glycerin in dilute solutions adds smoothness to drinks, and is often a recommended addition in place of sugars. Such an addition has several decided advantages, because not only does glycerin impart its pleasant sweet taste to the liquids but its presence tends to blend and harmonize the various flavors and odors which contribute so much to the palatability of the final product. Furthermore, unlike sugar syrups, glycerin solutions do not crystallize out in high concentrations or under adverse conditions.

A study of the relative preservative values of glycerin and sugar solutions definitely gives the better rating to glycerin. While these investigations were made in relation to certain official pharmaceutical syrups, the information obtained is readily applicable to flavoring syrups which are basically similar. The superiority of glycerin as a preservative was shown in every case. Such



solutions showed more resistance to oxidative changes than the official syrups. Sucrose syrups become inverted after a period, while the glycerin solutions remain clear and limpid. Glycerin also prevents precipitation in citrate solutions for over a month.<sup>4</sup>

Because of this preservative action, glycerin is used in flavorings and fruit-juice beverages. Illustrative of the latter application are the specifications of a basic patent for preserving the juices of citrus fruits. In this process, one part of glycerin is added to eight parts of the juice. Sugar and other preservatives, such as sodium benzoate may also be added.<sup>5</sup>

From the beverage aspect, however, probably no single property of glycerin is more important than its solvent power. This is an essential characteristic since the taste agents must not only be extracted from their plant sources, but must also very often be properly combined to produce the fullest effects. Glycerin aids in both of these processes. Glycerin also possesses the quality of dissolving essential oils, so that by adding it to a flavoring substance a great many more essential oils are brought into solution than would be by the action of water or alcohol.<sup>6</sup> DeGroote<sup>7</sup> points out that, "Glycerin has powerful solvent properties, it combines in this respect the properties of water and alcohol; and many substances dissolve even more easily in it than in either of the two liquids."

It may have been noted that the word, flavor, has been frequently used while the word, extract, has apparently been avoided. According to the U. S. Department of Agriculture definition, an extract refers to alcoholic preparations only. Nevertheless, glycerin is one of the few legally permitted additions to pure vanilla extract.<sup>8</sup> Many states, however, hold that the terms extract, flavor, flavoring, spirits, essence, and tincture as applied to solutions for flavoring food products are synonymous. As deGroote indicates, the Canadian standards for extracts are more explicit than those of this country and do not leave any doubt as to the important place of glycerin. The Canadian ruling reads, "The usual solvents employed in the preparation of flavoring extracts are ethyl alcohol, water and glycerin." The ruling further indicates that in the event that any solvent other than the above is used, it must be harmless to health and its presence stated on the label.<sup>9</sup>

One of the most generally known and accepted uses of glycerin is in the preparation of vanilla extracts. The fact is that glycerin, for many years, has been employed in connection with alcohol in making vanilla extracts. Glycerin is usually added with the object of giving sweetness and adding body and viscosity to the preparation. Vanilla extracts made with glycerin are darker in color, and some authorities are of the opinion that this is due to the added extractive and solvent power of this liquid. One simple formula for making vanilla extract given by Henley's text,<sup>10</sup> consists of:

Vanilla Beans (Good Quality) . . . . .	16 ounces
Alcohol . . . . .	64 fl. oz.
Glycerin . . . . .	24 fl. oz.
Water . . . . .	10 fl. oz.
Dilute Alcohol . . . . .	Sufficient

The ingredients are mixed and macerated with frequent agitation for three weeks, filtered and then dilute alcohol is added to make one gallon.

Compound vanilla extracts likewise contain substantial quantities of this solvent. Non-alcoholic vanilla flavors, in which glycerin is one of the chief agents, are readily available. Bennett<sup>11</sup> gives the following:

Vanillin . . . . .	3.2 g.
Coumarin . . . . .	0.19 g.
Glycerin . . . . .	180.0 ml.
Syrup . . . . .	180.0 ml.
Water . . . . .	120.0 ml.
Ether . . . . .	120.0 ml.
Color . . . . .	Sufficient

The vanillin and the coumarin are dissolved in the ether. The glycerin, syrup and water are mixed and the ether solution is added to this. The emulsion is beaten until the ether is entirely volatilized and then the color is added.

Flavoring pastes have become popular in the last few years and glycerin is an important ingredient of these non-alcoholic flavoring agents. Not only are vanilla pastes available, but other preparations, such as orange, lemon, almond and cinnamon products, are readily made by the same process.<sup>1</sup>

Powdered flavoring products have been available for use for many years. Recently they have been prepared, and have become

quite popular for home use to make soft drinks and for other food-flavoring and coloring purposes. Usually, these compounds consist of an essential oil incorporated with cane sugar and glycerin, although other flavoring and coloring elements could be used. In these glycerin serves as a vehicle and solvent for the essential sapid material and to aid distribution through the sugar. Kessler <sup>12</sup> presents a type formula for this class of product:

	Parts by Weight
Granulated Cane Sugar .....	65
Oil of Bitter Almonds .....	3
Glycerin, C.P. ....	2

The ingredients are thoroughly mixed and packed in paper-lined, air-tight containers.

Artificial fruit essences for flavoring purposes, made from synthetics are now widely used. These preparations are based on combinations of the aromatic primary substances which are found to be present in the natural fruits. In compounding these essences, considerable experience and care is essential. In the great majority of these compounds, glycerin is a constituent. As has already been indicated, glycerin appears to blend and harmonize the varied odors and flavors used. Almost every type of fruit, berry and nut essence preparation contains glycerin. The fluid is found in essences of such fruits as peach, apricot, plum, cherry, lemon, pear, orange, apple, grape and such berries as raspberry and strawberry. Formulas for making these flavoring essences are readily available in any standard formulary.<sup>1,10,11</sup> The following artificial strawberry essence will serve to illustrate these preparations:

	Parts by Weight
Methyl Salicylate .....	1
Acetic Ether .....	8
Butyric Ether .....	5
Nitrous Ether .....	1
Glycerin .....	2

The ingredients are mixed and 2 parts of the concentrated essence are added to:

	Parts by Weight
Alcohol .....	8
Water .....	10

Color may be added as desired.

It must not be assumed, however, that the usefulness of glycerin is limited to the manufacture of the artificial fruit essences, so widely used as drink flavorings. Glycerin likewise is an important ingredient of syrups made from natural fruits. The following is one method for making glycerin-containing fresh fruit syrups: The fruit is cleaned by washing with warm water and is then mashed in a large earthenware vessel. The pulp-containing vessel is put in a warm place to ferment. It should be stirred occasionally during the three or four days it is fermenting. The addition of 2% sugar will hasten this process. The juice is then drained off through a cloth and the marc is also pressed to obtain the fruit juices. This fluid is then set aside to permit complete fermentation and clarification. The juice should form a clear solution when mixed with two volumes of 90% alcohol. To make the syrup, each pint of clarified juice receives an addition of one ounce of glycerin and one and one half pounds of sugar. The extract is heated to dissolve the sugar and while still hot, poured to fill sterilized bottles, and sealed with an air-tight closure.

The popularity of chocolate drinks in this country need hardly be emphasized. Glycerin enters extensively into the preparation of all types of chocolate confectionery; soft drinks are no exception. As usual, glycerin lends smoothness and body and also aids in the distribution of the flavoring material. The following chocolate essence <sup>1</sup> is illustrative:

	Parts by Weight
Powdered Chocolate .....	20
Syrup .....	25
Glycerin .....	30
Distilled Water .....	15

The chocolate and the glycerin are triturated until a smooth mixture results, transferred to a porcelain dish, washed out with water and the whole boiled with constant stirring on a sand bath for five minutes. Then the syrup is mixed in, and when the preparation is cold, it is flavored with vanilla essence.

Coloring agents for soft drinks are readily dissolved in glycerin. This is an established, standard usage and is particularly valuable in making red coloring compounds with carmine and with cochineal. Methods for preparing these solutions are given in the

official "National Formulary VI" \* and have, therefore, wide application in all types of products. When glycerin is used in these coloring compounds, no preservative is needed.<sup>1</sup> A fine green color can be obtained by adding indigocarmine to a mixture of tincture of crocus and glycerin.<sup>10</sup> Permitted food colors are readily soluble in glycerin and prepared stock solutions of these can easily be made.

Heading or foaming is imparted to carbonated and other beverages by means of saponin-containing preparations. Glycerin is an agent in these products, which are known variously as foam, extract, gum syrup, liquid heading, etc. Older formulas for making foam extracts employ a menstruum of glycerin, alcohol and water, in which is macerated crushed soap bark. In more modern practices, a preparation of saponin is supplied by manufacturers to induce a rich foamy head to beverages. The following formula is given as an example of a heading liquid<sup>1</sup> for producing foam in soft drinks:

	Parts by Weight
White Saponin .....	$\frac{1}{2}$
Powdered Acacia .....	$\frac{1}{2}$
Glycerin .....	4
Water to Make .....	20

Another similar formula using a trade preparation, is given by Bennett:<sup>11</sup>

Saponin .....	1 lb.
Glycerin .....	$\frac{1}{2}$ gal.
Water .....	$\frac{1}{2}$ gal.

The saponin is dissolved in  $\frac{1}{2}$  a gallon of clear water then the glycerin is added. One-half dram to 1 gallon or 1 ounce to 15 gallons of syrup are used.

In the production of wines, glycerin remains in the beverage as an important flavor-contributing constituent and is, of course, a natural ingredient of such products.<sup>13, 14, 15, 16, 17, 18</sup> According to Perrody,<sup>5</sup> wine contains a certain amount of glycerin in its natural state, since the process of fermentation yields glycerin as well as

\* *National Formulary VI*, Washington, D. C., Am. Pharm. Assoc., 1936.

alcohol; the final content of glycerin being approximately 10% of the total alcohol content of the wine. This, however, is a variable figure with various types and kinds of wine and may also vary in any particular kind of wine, depending upon such factors as fermentation and alcoholic evaporation during storage and aging. Thus, it has been established that old wines kept in barrels and having a greater market value than new wines, are characterized by a higher proportionate glycerin content. Thus, Bertin,<sup>10</sup> in an analysis of twenty-five Mascara wines of known purity, found that the glycerin content varied from 6.7 to 15.7 grams per liter, and the ratio of alcohol to glycerin varied all the way from 8.3 to 16.4.

The alcohol-glycerin ratio in wines is often employed as a means of determining adulteration of wines. Since, as pointed out by Woodman<sup>11</sup> in his text on food analysis, the normal fermentation of sugars under the restricted conditions of wine making, produces a fairly definite proportion of glycerin to the amount of alcohol, this ratio is of much more importance than either constituent alone in determining whether alcohol has been added to wines. In some wine-producing countries, the limits of the alcohol-glycerin ratio have been fixed by law. It is a quite common procedure to add glycerin to wines to impart a finer taste and to improve mellowness and roundness.

The low freezing point of glycerin solutions has been utilized in processing certain wines. In the manufacture of champagne and other sparkling wines, for example, glycerin is employed in the "disgorging" process. In this procedure, the sediment and a portion of the liquid in the bottle neck are frozen solid by placing the neck in some liquid, which is usually glycerin, cooled to below 12°F. This readily permits the removal of the agrafe and the plug is forced out by the gas pressure in the bottle with but little loss of liquid.<sup>19</sup> Glycerin is widely used as a lubricant for refrigerating equipment and is also employed in the temperature regulating mechanisms of this equipment.

The formulation of base flavors for various types of liquors and liqueurs frequently utilizes the several advantageous qualities inherent in glycerin. The formulation of such flavor bases calls for both skill and experience and is comparable to the art of perfume compounding. Glycerin not only finds employment in making

many types of fruit flavors for liqueurs and such, but is likewise used as a vehicle in making flavors for stronger drinks, such as gin, essence of cognac brandy, essence of rock and rye whiskey, artificial Scotch whiskey flavors and others.<sup>20</sup>

A typical example is the following formula and procedure for making Holland gin:<sup>20</sup>

Oil·Gin .....	1000 ml.
Glycerin .....	200 ml.
Alcohol .....	216 oz.

Five ounces of the above flavor mixture are dissolved in  $2\frac{1}{4}$  gallons of alcohol. Then  $2\frac{3}{4}$  gallons of water are added. The gin is mixed and filtered through magnesium carbonate.

In mixing cocktails, the addition of a few drops of glycerin is one of the professional secrets of experts who know the value of this fluid to provide a smooth blend and prevent the separation of the ingredients. It also acts as a sweetener. A typical recipe of this type in which glycerin serves to make a smoother drink is the following method for making a "Southern Special":

Grenadine .....	1 oz.
Lemon Juice .....	$\frac{1}{2}$ oz.
Glycerin .....	1 Teaspoonful
Sugar .....	if Desired
White of .....	1 Egg
Gin .....	Small Whiskey Glass

All ingredients are combined and shaken well with cracked ice. The cocktail is strained before serving.

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148    *Glycerin—Its Industrial and Commercial Applications*

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## FOODS

WITH THE growing appreciation of the functions of glycerin as a safe and wholesome aid in commercial food processing, the diversity of its applications is broadening.

In many instances, it is employed as a preservative agent, in others for its solvent and extracting value, whereas some food processors employ glycerin in their products to maintain freshness longer, or to impart flavor or body. Usually, when glycerin is employed in foods, several or all of these properties are utilized simultaneously. Its natural sweetness, to which it owes its name (from the Greek word, *glykeros*) is a factor for the use of this fluid in foodstuffs.

One of the uses of glycerin is in connection with eggs, especially egg yolks. As Jacobs<sup>2</sup> points out, "Glycerol yolks are packed chiefly for the baking trade. They contain from 5 to 7% of glycerin and have the property of keeping the cakes fresh and moist for longer periods of time." Ovson<sup>3</sup> describes a method for conserving the goodness of eggs by sharp freezing. The addition of 5% by weight of glycerin to the yolks, he points out, prevents gummy, lumpy particles from forming in the baked products and also permits the yolks to thaw out smoothly. Yolks packed with glycerin give increased baking volume because of the affinity of glycerin for water. LeClerc and Bailey<sup>4</sup> also indicate that the addition of glycerin to eggs, prior to freezing, helps to maintain the emulsifying, lubricating and gas retention properties. Such additions also minimize the formation of large ice crystals and to a certain extent reduce the dehydrating action of slow freezing.

A patented British process<sup>5</sup> for preserving liquid egg materials employs glycerin together with water and a salt. After the desired neutrality or slight alkalinity of the mixture is obtained with the salt, part of the water is removed by a special drying apparatus to reduce the consistency to a creamy or pasty mass. American

patents<sup>6</sup> cover the use of certain glycerin esters, which, when mixed with eggs preparatory to freezing, serve to improve the texture and emulsifying properties of the egg material.

The Martin and Caulfield<sup>7</sup> investigations on ice cream mixes show that whole fresh eggs in amounts up to 4% and egg yolks up to 2% improve the whipping properties of the mix and the texture of the ice cream. The studies further reveal that egg yolks for ice cream manufacture may be suitably preserved and stabilized by the addition of 5% of corn syrup, 1% of glycerin, and 0.5% of gelatin and stored at 0–10°F. The ice cream made from such stabilized yolks whips faster than mixes containing yolks not so stabilized.

Glycerin is also finding other use in ice cream production,<sup>8</sup> in solving the problem of making a fine quality ice cream with low carbohydrate content. Corbett and Tracy<sup>9</sup> found that when the sugar, ordinarily about 15%, is eliminated from the low-carbohydrate ice cream formula, the body is somewhat coarse and the high freezing point of the mix causes the cream to freeze to the inner surface of the freezer. To overcome these objections, glycerin was added; the optimal quantity is about 4% and this proportion lowers the freezing point about as much as does 15% of sucrose.

This lowering of freezing point was utilized in a patented process which advocates the addition of glycerin to mixtures containing milk solids, ice cream mix, and flavoring to prevent solidification at ice cream storage temperatures.

Glycerin is a frequent ingredient of shortening and other preparations used in baking, but most of the combinations are protected by patents.<sup>11</sup> A plastic shortening especially suited for cakes containing more sugar than flour is prepared, according to Coith and his co-patentees,<sup>12</sup> by steam-deodorizing a hard fat, adding an amount of glycerin sufficient to produce a synthetic fat containing not less than 19% of combined glycerin. This is mixed with a softer edible fat consisting essentially of triglycerides as the plasticizer. Another patent granted to these same workers,<sup>13</sup> similarly covers a shortening preparation in which glycerin is one of the recommended substances.

Other shortenings for producing chemically leavened sweet baked goods with larger proportions of sugar than flour, are made

by causing a triglyceride fat to react with glycerin to produce an excess of combined glycerin.<sup>14</sup> Among the vegetable oils with which glycerin is employed to make these preparations, there may be included cotton seed oil, sesame seed oil and soybean oil. Various types of animal fats are also treated with glycerin. Glycerin and glycerin combination products are frequently employed as rancidity-preventing agents.<sup>15</sup> Royce holds patents covering the production of edible fatty acid esters made from cotton seed oil and glycerin. The two patents vary slightly in the method of producing these esters. In addition to the oil and glycerin, one process<sup>16</sup> uses certain fatty acids, and the other<sup>17</sup> employs small proportions of concentrated phosphoric acid. Many other processes that employ glycerin or glycerin derivatives for making shortenings and kindred products used in baking are listed in the recent patent literature.<sup>18, 19, 20, 21, 22, 23</sup>

The dairy industry, too, has found many uses for glycerin. Davis<sup>24</sup> advocates the use of alcohol-glycerin rennets in the making of cheese. He points out that, although bacterial and chemical analysis and graders' reports fail to distinguish the alcohol-glycerin rennet cheese from the brine-rennet cheese, the marked qualities in body and texture during the making of the alcohol-glycerin rennet curd and the sterility or low count of the alcohol-glycerin extract warrant further trials under practical conditions. Where brine-rennet may be suspected to be the cause of bacterial faults, the alcohol-glycerin rennets could well be used in its place, asserts Davis. These rennets also have superior keeping qualities as compared to the brine-rennets.

Several years ago, Gates et al.<sup>25</sup> received a patent for a process for preserving milk products such as milk, dried milk, cream, butter and the like. An addition of about 1.5% of glycerin is made to prevent rancidity in these products. The use of glycerin, in a 30% concentration, was shown to be a successful preservative for milk specimens to be examined for hemolytic streptococci, a group of pathogenic bacteria.<sup>26</sup> A formula for an inedible protective coating for foods, especially cheeses, consists of lactic casein 100, sodium borate 16, sodium bicarbonate 32, glycerin 34, gelatin 8 and distilled water 820 grams. This may be applied directly to the food or to the tin or aluminum used for packaging the food.<sup>27</sup>

Glycerin also has uses in the dairy laboratories. A modification of Grossfeld's test for determining adulteration of butter with coconut and palm kernel oil employs glycerin.<sup>28</sup> A 10% solution of glycerin in water has been highly recommended as a cooling medium for determining the freezing point of milk samples.<sup>29</sup> Maier<sup>30</sup> studied the advantages of using a 20% glycerin addition to sulfuric acid of 1.84 specific gravity. Results obtained were comparable to those found with the use of the straight acid in the Gerber test. The special advantage of this glycerin-acid combination is that it is much less corrosive to hands, clothing and the like than the acid.

When lecithin is added to margarine, this addition is best made, according to one patent,<sup>31</sup> in a lecithin-oil-glycerin combination. Glycerin is, however, finding use as a constituent of edible emulsions for use in foodstuffs. These emulsions are suited for use in margarine, cake batters, shortenings and the like. In one patented procedure,<sup>32</sup> salt, coloring matter, etc., may be added at any stage. The emulsifying agent is made by treating 100 parts of a special emulsion oil with 30 parts of glycerin, then mixing, stirring and heating in carbon dioxide. According to another patent,<sup>33</sup> a stabilizing agent for plastic emulsions, such as margarine or the like may be prepared by the reaction of glycerin with polymerized soybean oil. Somewhat similar is a British process<sup>34</sup> for making an emulsifier for use in the manufacture of margarine, cake batters, or shortenings. The emulsifying agent is made by polymerizing water-free glycerin, and heating the product thus formed with soybean oil to esterify the polymerizate. The glycerin polymerizate may be replaced by glycerin condensate, and other fats or oils may be used instead of soy bean oil. One European authority<sup>35</sup> points out that the necessity for having a hydrophylic group and a lipophylic group in an effective margarine emulsifier brings out the desirability of polyglycerin as a component.

Coloring materials for use in foods are frequently compounded with additions of glycerin.<sup>36</sup> Masurovsky<sup>37</sup> states that, in case a food color solution is to be kept for any length of time, it is advisable to add 10% of alcohol or 25% of glycerin (32 oz. per gallon of water) by volume.

Glycerin finds frequent employment in gelatin desserts since it prevents excessive drying and subsequent loss of desirable ele-

ments. One patented flavoring mixture, particularly suited to gelatin desserts and so compounded as to prevent the loss of the more volatile substances, may contain glycerin as the hygroscopic agent.<sup>38</sup> In another procedure, glycerin is listed as one of the suitable flavor improvers for preparing a gelatin product. Further specified treatment results in a reasonable dry, relatively stable and non-hygroscopic, free-flowing, flavored product.<sup>39</sup>

Glycerin-gelatin mixtures are standard combinations for making jujubes, soft pastiles and other jelly-like candies.<sup>40</sup> Since it prevents drying, graining and brittleness, glycerin is often included in other candies and confections.<sup>41</sup> One fondant formula specifies the inclusion of glycerin as a grain retarder.<sup>42</sup> Candies containing dried yeast also include glycerin.<sup>43</sup> Glycerin is also an addition to shredded coconut to keep it fresh and moist, and it is employed in the treatment of nuts and nut meats.<sup>44</sup>

Pectin is an essential constituent of jellies, jams and similar conserves. If it is not naturally present, it must be added. Adams' <sup>45</sup> tests have shown that dry, powdered pectins give better results as regards to flavor, color and the keeping qualities of the jams. Glycerin is often used in the preparation of these dry pectins.

A general method, used in several patents, consists in applying pectin solutions in thin layers to drying surfaces and then removing them as films. Here, glycerin acts as an agglutinating agent for the pectin. Some methods remove the glycerin from this jelling agent by means of alcohol.<sup>46</sup> More recently, glycerin has been employed to protect pectin-containing material against deterioration. According to this patent,<sup>47</sup> loss of jelly units from pectin raw material, such as apple pomace, is prevented by soaking the material in about 4% of aqueous solutions of glycerin and then drying the material.

Since its presence helps to prevent tough, dried-out fruit sections from forming, glycerin is employed in the manufacture of jams and preserves. One patented procedure, suitable for the preparation of marmalade and such, requires desiccation of the fruit juice with added anhydrous dextrose, thus forming a thick plastic body, into which are incorporated pieces of fruit that have been impregnated with glycerin.<sup>48</sup>

Some of the newer preserving processes for meat, fish and the

like use glycerin. These preparations, most of which are patented, may be in the form of salts, coatings, casings or similar additions. Frequently they are used to impart flavor as well as to preserve. One such seasoning agent is a solid composition containing salt mixed with small proportions of lecithin, oleoresins such as those of capsicum or ginger, glycerin, and an acid-neutralizing substance, such as calcium carbonate or the like.<sup>49</sup> Curing salts for meats, obtained by spraying concentrated salt solutions on heated drying rolls, are treated with glycerin to prevent caking.<sup>50</sup> In one patent it is claimed that meat may be preserved without any material change in color, if at the time of slaughtering and dressing, the meat is cut to the desired size pieces and covered with a fabric and a coating containing water, gelatin, glycerin and a small proportion of an essential oil, such as oil of cloves.<sup>51</sup> Glycerin also enters into the coatings and casings used for hams, sausages, etc.<sup>52, 53</sup> Food packaging materials are sometimes given added protective properties by means of coating or impregnating compounds containing glycerin.<sup>54, 55</sup> This fluid has also been advocated for use in processes for preserving bread.<sup>56, 57</sup>

One patent covers a method for preserving whale meat and similar foods containing fish oil. These are prepared and made palatable for human use by treating the flesh for several days in a 70 to 90% glycerin solution, to which small quantities of dissolved gelatin or agar-agar may be added. One to 10% of certain salts may be added to the glycerin or to the meat to lessen the sweet taste of the glycerin.<sup>58</sup>

In freezing foods to preserve their freshness and flavor, glycerin is playing an increasing role. In 1933, Davidson<sup>59</sup> described an apparatus for freezing fruits and fruit juices which employs glycerin as the refrigerant and lubricant. Later Bland<sup>60</sup> patented a process for preserving perishable foodstuffs such as meats, fish, fruits, etc., by rapid freezing. These materials are immersed in a liquid chilling medium cooled to at least  $-30^{\circ}\text{C}$ . This chilling medium consists of pure glycerin 20–40%, alcohol 20–40% and water 25–45%. Methods are also given for repurifying this solution by filtration so that it may be reused continually. The suitability of glycerin as an immersant refrigerant for quick freezing of foods has been indicated in the report of Woodroof of the Georgia Experiment Station.<sup>61</sup>

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## MEDICINE AND SURGERY

GLYCERIN HAS a well-established and valued role in the field of medicine, serving in countless ways to improve or facilitate the administration of drugs and hasten healing.<sup>1, 2</sup> In addition to its use in official and non-official products of all types, in the laboratory, the hospital ward, in the preparation of vaccines, antigens and a host of other medical necessities, glycerin is an outstanding prescription item. This is clearly evident in prescription surveys made a decade apart.

A government-sponsored drug store survey in a metropolitan area before the war showed that glycerin ranked twelfth among official chemicals listed in the order of their frequency of prescription.<sup>3</sup> In a more recent survey, that of Plein and Risig<sup>4</sup> in 1942, glycerin held position number 14 among official chemicals used in 9,473 prescriptions. It held rank number 16 in competition with all medicines, including official and proprietary medicines. Of course this did not include many of the preparations in which glycerin was an important ingredient.

Classified as both a demulcent and emollient, glycerin finds extensive use as a vehicle for many drugs applied to the skin.<sup>5</sup> Equally important, however, is the frequent employment of glycerin as a vehicle or solvent for internal medicaments and for the preparation of parenterally administered products. It likewise plays an essential part in the manufacture of vaccines, as in the preparation of smallpox vaccine, in tuberculins, such as are employed in the Volmer patch test,<sup>6</sup> and in the extracts used for testing and treating allergy,<sup>7, 8</sup> as well as numerous other related products.<sup>9, 10</sup>

The physiology of glycerin is well established and it is recognized that glycerin is a normal digestion product resulting from the natural assimilative breakdown of fats. The extensive in-

vestigations done under the direction of the famous physiologist Anton J. Carlson <sup>11</sup> have shown the safety of glycerin for internal use.

Some of the more prominent functions of glycerin in pharmaceutical and medicinal preparations have been aptly summarized by Prinz.<sup>12</sup> Glycerin, he reports, serves to: (a) give a certain viscosity or body to liquid preparations, (b) prevent enzymic changes, particularly fermentation of liquids, (c) act as a solvent for drugs, and (d) prevent drying out of ointments, creams, pastes, and similar products.

Glycerin is outstanding as a solvent for medicinal substances; often being much more effective than other solvents. By the use of glycerin it is possible to prepare highly concentrated medicinal solutions. Special preparations of this nature are known as "glycerites." The solvent properties of glycerin are widely utilized in the extraction of drugs, of biologicals and of glandular products.

The value of glycerin as a vehicle was repeatedly stressed by the late Dr. Bernard Fantus <sup>13</sup> of the Cook County Hospital, Chicago. His glycerin-containing solutions of barbital, soluble phenobarbital, potassium citrate and acetyl-salicylic acid have enjoyed wide popularity as prescription items.

As new materials or methods are developed in medicine, it will often be found that use of glycerin either improves the method or facilitates its application. The tannic acid method for treating burns offers an excellent example. Tannic acid jellies and related burn preparations almost invariably employ glycerin as an essential ingredient. Indeed British studies <sup>14</sup> of tannic acid burn jellies have shown that the most satisfactory preparation is made by incorporating tannic acid into a tragacanth glycerin base; the final product contains 20% of glycerin.

The war has shown that tannic acid therapy has definite limitations and it is now known that such products should never be used on the face, hands and flexures. Newer types of burn treatments, designed to overcome the disadvantages of tannic acid have been evolved, and glycerin has found wide utilization in the formulation of these newer items. As a matter of fact, sterile glycerin alone is very frequently employed in treating burns of the face and hands.<sup>15</sup>

Where dyes are employed in the treatment of burns, glycerin frequently finds favorable use in the vehicles used to apply these newer effective agents. A case in point is a spray, suggested by the Department of Health for Scotland,<sup>16</sup> which has been tentatively recommended in the case of burns of the air passages, e.g., the mouth, larynx, nostrils, as well as trachea and bronchii.

A glycerin-containing preparation, designed to meet the high specifications of the National Research Council for a tannic acid-sulfadiazine burn jelly, uses a sulfonamide.<sup>17</sup> A somewhat similar sulfonamide-glycerin burn paste, called "Euglamide," developed in England,<sup>18</sup> has received considerable attention both in that country and in the United States. However, glycerin is being used with ever-increasing frequency in preparations for the local application of sulfonamides, not only for the treatment of burns, but in dermatological affections and wounds.

The value of glycerin as a vehicle for these comparatively new vital drugs has been demonstrated in many ways in both the laboratory and in actual practice. The studies of Locatelli and Bowden,<sup>19</sup> in which the bacteriostatic action of sulfanilamide in various media were determined, showed that the activity of the sulfa drug in a 30% concentration was greatest (even greater than that of the powder itself) when dispersed in glycerin.

These findings have been corroborated in practice by the observations of the dermatologist, Lain.<sup>20</sup> He found that a super-saturated solution of sulfanilamide in glycerin (4-8 g. sulfanilamide powder in 30 ml. of slightly warm glycerin) "has proved so successful and gratifying that it has now come to be used as a routine treatment in the state university clinic and in the private practice of my associates and myself in all cases of impetigo, acute infectious dermatitis of the ears, scalp or feet, coccigenic sycosis, folliculitis, septic ulcers and other streptococcic and staphylococci infections." He, too, found that no other vehicle gave such rapid and satisfactory results as those obtained with the glycerin-sulfanilamide preparation.

In England, Perrins<sup>21</sup> states that 5% sulfonamide in glycerin (or a mixture of glycerin in water) is being prescribed as a dressing in skin diseases.

In their studies of emulsion bases for the local treatment of pyogenic cutaneous infections with sulfathiazole, Pillsbury and

his associates<sup>22</sup> found that a glycerin-containing base was the most effective product for such therapy. A glycerinated base served as the medium for the sulfanilamide-allantoin combination used by Veal and Klepser<sup>23</sup> to obtain remarkably good results in the therapy of surgical infections.

It may be mentioned that 10% of glycerin is included in both the medium and thin emulsion bases listed in the new "Manual of Dermatology" prepared for use by military physicians, under the auspices of the National Research Council.<sup>24</sup> These emulsion bases are intended as media for applying various medicaments in treating dermatological conditions.

Glycerin and glycerin-containing preparations have long been employed as a standard, effective vehicle for antiseptics, but the newer medical literature indicates a growing utilization with such agents as iodine,<sup>25</sup> dyes,<sup>26</sup> acriflavine<sup>27</sup> and the like.

It should also be mentioned that glycerin has definite antiseptic properties of its own, when used in a suitable concentration.<sup>1</sup> This fact, plus the lymphagogue action and other desirable effects of glycerin, form the basis for Smith's<sup>28</sup> use of this fluid in the prevention of wound infection and in the treatment of infections and surgical conditions. According to one report,<sup>29</sup> infected wounds are found to respond well to a thorough cleansing with alcohol, followed by packing with sterile gauze saturated in glycerin.

An effective, inexpensive liquid for the sterilization of instruments consists of a 2% compound cresol solution and 5% glycerin in a mixture of equal parts of alcohol and water. According to Novak,<sup>30</sup> this solution kills all pathogenic organisms in one minute or slightly longer, it is much less expensive than commercial preparations used for sterilizing knives, scissors and other instruments and, in addition, inhibits rusting.

Pastes and ointments for treating dermatological conditions, wounds and other infectious conditions, utilize the several advantageous properties of glycerin. Especially useful and widely employed are a series of pastes developed and described by Fantus and Dyniewicz<sup>31</sup> and glycerin is an ingredient of a large proportion of these.

The urea (carbamide) paste, the tragacanth-benzoic acid paste and the pectin paste, all of them containing glycerin, have proven

their efficacy in nursing care and in the treatment of bed sores.<sup>32</sup> Urea, a safe, inexpensive deodorant and healing substance, practical for use in the home care of cancer patients is best employed in the form of a glycerin-containing paste.

Glycerin, alone or in simple combination with other standard medicinal preparations or readily available materials, finds numerous direct uses in nursing care or hospital tasks. Thus glycerin, mixed with equal parts of water or lemon juice, is used to wipe the tongue and lips during fevers and to overcome the dry sensation in the mouth. A preparation of lemon juice in glycerin, applied with a swab, cleanses the mouth and sweetens the breath. Such a preparation has been advocated in nursing care in nephritis,<sup>33</sup> in scarlet fever,<sup>34</sup> in the delivery suite<sup>35</sup> and elsewhere.<sup>1</sup>

As an enema, glycerin in a teaspoonful quantity may be injected into the rectum to provide an efficient and rapid action. Dilution with equal parts of water permits one to three ounce quantities to be used.<sup>1</sup> Of course glycerin suppositories may also be used. The so-called "two-four-six enema" is often used and is quite effective,<sup>36</sup> consisting of:

Magnesium Sulfate .....	2 oz.
Glycerin .....	4 oz.
Water .....	6 oz.

When a rectal thermometer is used, a little glycerin not only facilitates its insertion, but by its action on the rectal muscles further assures its retention. In passing, it might be mentioned that glycerin is a basic constituent of catheter and instrument lubricants.<sup>37</sup> Unlike oily lubricants which cause deterioration of the rubber tubing, glycerin actually serves to maintain the usefulness, flexibility and resilience of such essential rubber instruments. This is a fact established by the careful studies of Aquadro and Barbour<sup>38</sup> in 1938.

Glycerin also finds use in the care and recovery of all-glass hypodermic syringes. For example, if glass surfaces of syringes have become "frozen" or locked, these valuable instruments need not be discarded. Very often the plunger can be separated by merely boiling the frozen syringes in an aqueous solution containing 25% of glycerin.

Of course, glycerin is an excellent preventative against syringe "freezing" during storage and it has the advantage that it can be washed away with water before sterilization or use. Indeed, lubrication and sterility can be achieved in one simple method.

According to Tomb,<sup>39</sup> a British authority, a mixture of equal parts of 90% alcohol and glycerin of phenol (equivalent to Glycerite of Phenol U.S.P.) forms a safe and effective means of storing syringes that have been sterilized by boiling. Tests have confirmed both the safety and efficacy of this procedure. When the syringe is taken out of this mixture, the alcohol evaporates quickly, leaving behind a thin film of glycerin of phenol which serves not only to keep the interior of the barrel sterile, but also prevents the piston from sticking.

Glycerin has long been valued for its efficacy in preparations for treating ear affections. Thus, warm glycerin alone, placed dropwise or in cotton, will often relieve earache.<sup>40</sup> The use of phenol in glycerin drops is a standard procedure for relieving pain,<sup>41</sup> and in addition they help to sterilize the meatus before the drum ruptures in cases of acute otitis media.<sup>42</sup> Other drugs, such as boric acid, iodine, ichthyol, etc., may also be incorporated in glycerin as required.<sup>40</sup>

A few drops of glycerin in the external ear canal will often serve to soften the wax and loosen other accumulations.<sup>1</sup>

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## ORTHODONTIA AND DENTISTRY

IN MODERN dentistry, the useful application of glycerin in such standard dental materials as antiseptics, polishing materials, disclosing solutions, molding materials, root pastes, dentifrices, mouth washes and the like<sup>1</sup> has been greatly extended to many new processes and materials.

Although glycerin itself has decided germicidal properties against many pathologic organisms, it finds its widest use as a solvent in the preparation of many widely used dental antiseptics such as Talbot's iodoglycerole and other glycerin-iodine combinations, glycerite of phenol and others. Special antiseptic preparations, such as those used in preoperative and post-operative oral surgery, generally contain this versatile fluid. A typical instance is the preoperative solution described by Gross<sup>2</sup> in his articles on dental surgical procedures. He employs the following solution to apply to the mucous membranes and operatives area:

Iodine Crystals .....	24 gr.
Oil of Wintergreen .....	24 min.
Glycerin, q.s. ad .....	8 oz.

This solution is practically identical with Henahan's solution, which Hurst<sup>3</sup> recommends as a swabbing preparation for the mouth in cases where immediate dentures are applied after surgical intervention.

Similarly, glycerin finds extensive use in the preparations employed for the treatment of specific oral diseases, such as the various forms of gingivitis, Vincent's angina, and the several types of stomatitis. Thus, glycerite of tannic acid, a few drops in warm water, forms a standard mouth wash for the after-treatment of pyorrhea. Another preparation<sup>4</sup> for the same purpose, to be diluted with five parts of warm water before use, consists of:



Potassium Chlorate .....	30 g.
Glycerin .....	30 ml.
Phenol .....	60 ml.
Water, q.s. ad .....	250 ml.

Talbot's iodine-glycerin solution finds extensive use in the treatment of gingivitis, as do alkaline, glycerin-containing mouth washes, such as the following,<sup>4</sup> which is diluted as required:

Sodium Borate .....	2 g.
Sodium Chloride .....	2 g.
Glycerin .....	45 ml.
Wintergreen Water, q.s. ad .....	180 ml.

Neosarsphenamine in glycerin (generally a 10% solution) is a standard preparation for the treatment of that often recalcitrant condition Vincent's angina or trench mouth. However, other preparations for the therapy of this all-too-frequent oral disease take advantage of the several properties inherent in glycerin. One widely prescribed product of this type, to be used as a mouth wash four times a day diluted with a small amount of water<sup>5</sup> generally consists of:

Solution of Potassium Arsenite .....	4 ml.
Glycerin .....	30 ml.
Wine of Ipecac .....	4 ml.
Hydrogen Peroxide, to Make .....	90 ml.

Others, prefer to use a mixture of equal parts of liquor arsenicalis, wine of ipecac and glycerin. With this last preparation, it is reported that foul breath disappeared rapidly, indeed astonishingly, as did the sore and bleeding gums, the ulcers and the generally inflamed appearance of the mucous membrane of the mouth.<sup>6</sup>

The formula of the oxidizing mouth wash recently recommended by Francis<sup>7</sup> during the treatment for Vincent's angina is as follows:

Fowler's Solution .....	6 oz.
Glycerin .....	4 oz.
Hydrogen Peroxide .....	½ gal.
Distilled Water, to Make .....	1 gal.

Sufficient anhydrous copper sulfate (to reduce fungus ac-

tivity) is added immediately before dispensing to make a 0.1% solution. Francis suggests that use of a No. 4 capsule filled with copper sulfate to facilitate preparation of this solution; the amount being sufficient for 8 oz. of the wash.

Williams<sup>8</sup> points out that many caustics, including copper sulfate made as a paste with glycerin, have been used in the treatment of Vincent's disease. He, however, prefers the application of an iodine solution used in conjunction with a 20–35% aqueous solution of silver nitrate. The iodine may be used either as an alcoholic, aqueous or glycerin solution, the formula for the last being:

Iodine Crystals .....	20 g.
Zinc Iodide .....	12 g.
Water .....	8 ml.
Glycerin .....	40 ml.

Two dishes are required, one containing the iodine solution, the other the silver nitrate solution. A pellet of cotton wool is saturated in the iodine, and with tweezers squeezed over the area. This is followed by similar treatment with silver nitrate.

Most dentists are familiar with the use of glycerite of boro-glycerin and of glycerin-containing Bowman's solution for the treatment of stomatitis. This last consisting of:

	Parts by Volume
Solution of Arsenous Acid .....	12
Tincture of Ipecac .....	12
Glycerin .....	8

is applied locally in the treatment of ulcerative stomatitis.<sup>4</sup>

Another familiar preparation, in which glycerin is a major ingredient, for use in cases of stomatitis and thrush is honey of rose and sodium borate N.F. VI.<sup>9</sup> The following solution, to be frequently used as a mouth wash or applied by means of cotton swabs, has been recommended for use in catarrhal, vesicular or ulcerative stomatitis:<sup>4</sup>

Potassium Chlorate .....	4 g.
Solution of Hydrogen Peroxide .....	30 ml.
Glycerin .....	30 ml.
Water, q.s. ad .....	120 ml.

In dentistry, as in other fields of modern medicine, the outstanding value of the topical application of sulfonamides in conjunction with glycerin is being frequently utilized. Particularly indicative was the brief report published by DeWolf in 1940.<sup>10</sup> In his clinical studies, a sulfanilamide paste (made by mixing 2 grains of sulfanilamide with distilled water) was placed in the socket after extraction and partial swabbing to remove the blood. This was followed by the insertion of a cotton pledget moistened with 10% guaiacol in glycerin as it overlay the sulfanilamide paste.

In fifty patients so treated, the dry socket developed in only four instances. Moreover, healthy granulation tissue was seen to have begun to develop within two days. This was in marked contrast to fifty control patients not given this treatment, but handled in the usual way. In these latter cases, eighteen developed dry socket, and pain persisted for two to three weeks.

"That the use of sulfanilamide with guaiacol in glycerin has such amazing results," concluded DeWolf, "is very interesting. From my observations, guaiacol in glycerin alone does not approach the efficiency it has when used in combination with sulfanilamide, nor does sulfanilamide alone prove nearly so efficient as when the combination is used."

More recently, Meacham and Osgood,<sup>11</sup> working with sulfathiazole, suggested that this efficient sulfonamide might be more efficiently applied by using a suspension of the powder in dentistry and oral surgery. Among the methods advocated by these authorities was the mixing of the sulfathiazole powder with chemically pure glycerin. By such means a mixture is made which can easily be injected into infested wounds, sockets or incisions, and, moreover, the powder is held in suspension without any apparent inhibition of its action.

Glycerin has long been a standard ingredient of root canal preparations.<sup>12</sup> This use has been further extended during recent years. Interesting in this connection is the modification of Rickert's root sealer powder (used in conjunction with a glycerin-iodine solution) advocated by Easlick and his associates.<sup>13, 14</sup> In its modified form, this contains:

	Parts by Weight
Zinc Oxide .....	14.8
Thymol .....	2.0
Powdered Rosin .....	3.0
Paraformaldehyde .....	0.3

This is used in combination with the following preparation:

	Parts by Weight
Iodine Crystals .....	0.3
Glycerin .....	15.0

All the ingredients are heated on water bath until solution is effected.

Mention should also be made of the canal filling paste recommended by MacLeod<sup>15</sup> in his discussion of "*Accidents to Children's Teeth*," which consists of:

	Parts by Weight
Zinc Oxide .....	15
Tribromphenate .....	5
Phenol .....	$\frac{1}{2}$
Glycerin, Sufficient to Make a Paste.	

"Disclosing solutions" offer further examples of the standard use of glycerin in dentistry; Skinner's disclosing solution being a typical instance. This, incidentally, has been modified by Glass<sup>16</sup> who uses the following:

	Parts by Weight
Iodine .....	3.3
Potassium Iodide .....	1.0
Zinc Iodine .....	1.0
Glycerin .....	20.0
Water .....	20.0

A distinct departure from iodine-containing disclosing solutions is the following preparation employed by Easlick<sup>14</sup> in dentistry for children:

Bismark Brown .....	0.3 g.
Alcohol .....	10.0 g.
Glycerin .....	120.0 g.
Oil of Anise .....	1.0 Drop

In passing, it might be mentioned that dyes are also used in the glycerin-containing disclosing solution patented by Bender in 1939.<sup>17</sup>

Disclosing solutions, of course, merely serve, by aiding detection of mucin or bacterial plaques, in the cleansing of teeth. However, in these cleansing processes, glycerin has also proven its worth, generally as a suitable suspending medium for the various abrasive materials. A preparation of this type, for use in children's dentistry,<sup>14</sup> can be made from:

Flour of Pumice .....	70.00 g.
Borax .....	30.00 g.
Glycerin .....	75.00 g.
Carmine .....	0.25 g.
Oil of Spearmint .....	0.1 Drop

Hanke,<sup>18</sup> however, has reported that plaques disappear from teeth that are given ordinary care, provided the mouth is also rinsed once or twice each day with certain antiseptic solutions. The one recommended by Hanke, containing a special organic mercurial, is made as follows:

To 4 gallons of distilled water are added 2880 ml. of U.S.P. glycerin, 30 ml. of 1 N sodium hydroxide, 90 g. of C.P. sodium acetate, 450 ml. of a 1% solution of sodium parahydroxy mercuribenzoate, and 30 ml. of a 10% solution of oil of peppermint in alcohol. This is diluted with distilled water to 5 gallons. (To prepare the 1% mercurial solution required in the above formula, 10 g. of sodium parahydroxy mercuribenzoate, 10 g. of C.P. sodium acetate and 5 ml. of 1 N sodium hydroxide are mixed with sufficient distilled water to make 1000 ml. of solution.)

It is claimed that this glycerin-containing mouth wash is free from such undesirable effects as discoloration of the teeth, amalgamation with gold fillings, or a metallic taste.

To the technician who works from impressions supplied by the dentist, it is of interest that glycerin is a frequent ingredient of modern impression materials. A typical modern dental impression "wax"<sup>19</sup> can be made from:

	Parts by Weight
Shellac .....	45
Talc .....	30
Glycerin .....	2½
Coloring .....	Sufficient
Tallow Fatty Acids, to Make .....	100

Glycerin likewise enters into the formulation of dental imprint compositions, some patented, with agar-agar,<sup>20, 21</sup> waxes<sup>22</sup> or resilient vulcanized rubber filaments<sup>23</sup> as the base.

Glycerin is frequently included in the preparation of molds and molding compositions used by the dental technician. The dental authority, Prinz<sup>24</sup> has included several such items in his standard "*Dental Formulary*." According to Prinz, 'Moldine' is made by mixing pure dry clay with sufficient glycerin to make a plastic mass. Hardened moldine can be restored to a workable condition by placing it in a vessel and covering the mass with a solution of:

	Parts by Weight
Glycerin .....	1
Water .....	9

The mixture is allowed to boil, with constant stirring, until the water has evaporated.

The following method for making molds for duplicating plaster casts from original casts or models is indicative and typical:

	Parts by Weight
Carpenter's Glue .....	20
Gelatin .....	20
Glycerin .....	35
Water .....	25
Cottonseed Oil .....	20

The glue, gelatin, and water are placed in an enamelled double boiler and let stand for twenty-four hours. Then they are heated until the ingredients are dissolved and the glycerin and oil are mixed in.

To use this mixture, the dry talc-coated model is placed in the molding flask and the warm mixture is poured over it. This is allowed to stand until perfectly hard, and then the cast is carefully removed from the elastic mold. According to Prinz, a number of casts may be obtained from the same mold.

Another glycerin-containing formula given by Prinz is for an elastic compound for crowns and plate swager. Its constituents and preparation are quite simple:

	Parts by Weight
Gelatin .....	250
Zinc Oxide .....	175
Glycerin .....	400
Water .....	300

The zinc oxide is mixed with 200 parts of glycerin to form a smooth paste. The gelatin is boiled in the water and in the remaining glycerin until it is dissolved and then the zinc oxide paste is stirred in. After 12 hours, the mass becomes solid and resembles unvulcanized rubber.

Useful, too, is the following method for making molding sand:

	Parts by Weight
Fine Quality Molder's Sand .....	3
Powdered Clay .....	1
Mix with:	
	Parts by Weight
Glycerin .....	1
Water .....	2

According to one patent,<sup>25</sup> glycerin is an essential constituent of a newer-type dental thermoplastic molding composition. In this process, glycerin is combined with rosin, aluminum stearate, rosin oil, triethanolamine stearate and wood flour.

Glycerin also is a recommended ingredient in a molding press lubricant by the use of which the removal of molded articles can be facilitated.<sup>22</sup> This lubricant consists of:

	Parts by Weight
Salt .....	20
Water .....	70
Alcohol .....	10
Glycerin .....	10

Glycerin is also suggested as an effective lubricant for the glass tubes used when casting sticks of sticky wax, inlay impression wax, and similar items. It is applied by pushing a glycerin-saturated cotton swab through the tube. Glycerin is also used to prevent sticking when making sheet wax.<sup>23</sup>

Moreover, glycerin as such, because of its oily feel and viscosity, makes an excellent lubricant for general laboratory use.

A mixture of glycerin and graphite may be used for similar purposes, and also serves as an excellent static-eliminator when applied to machine belts and the like. Although glycerin alone has such properties, a machine oil <sup>26</sup> that is resistant to organic solvents, that are so detrimental to ordinary lubricants, can be made from:

	Parts by Weight
Oleic Acid .....	100
Glycerin .....	50

As a suspending or massing medium for dental laboratory abrasive and polishing agents, glycerin is frequently used. Not only has this fluid sufficient body to carry the abrasive well, but it also has the advantage of being easily removed with water. Abrasive mixtures are readily prepared by mixing pumice, of the required fineness, with sufficient glycerin to form a mixture of the desired consistency. A polishing agent can be made by employing powdered chalk or stannic oxide with glycerin. One technician <sup>27</sup> has found that a fine gloss can be imparted to dentures by brushing them with a little glycerin and rubbing them briskly with a dry cloth after polishing. Glycerin, of course, is a standard ingredient of artificial denture polishes. It might also be mentioned that glycerin is often employed to maintain the flexibility of adhesives used in the manufacture of abrasive sheets,<sup>28</sup> and as a massing material in the formation of abrasive wheels.<sup>29</sup>

These properties of glycerin are also employed in restoring the abrasive quality of the mortar and pestle used for mixing amalgam which has become too smooth for proper amalgamation. To etch both the mortar and pestle, a little carborundum powder mixed with glycerin is placed in the bottom of the mortar and, then, using the pestle, the carborundum is rubbed, applying quite a bit of pressure.<sup>30</sup>

Glycerin has many other uses, too, in connection with dental laboratory material. It has long been advocated as a suitable quenching medium for steel, since it has properties intermediate between oil and water.<sup>31</sup> Standard procedures employ glycerin for hardening and tempering this metal.<sup>32</sup> For similar reasons, this fluid is also used in dental laboratory solutions for tempering other metals. The following copper-tempering solution,<sup>23</sup> is illustrative of this application:



	Parts by Weight
Concentrated Hydrochloric Acid .....	5
Ammonium Chloride .....	10
Sodium Chloride .....	50
Glycerin .....	800
Water .....	1000

In repair or restoration work, glycerin is used to remove teeth from vulcanite dentures. This is done by heating the plates in glycerin at its boiling point. The teeth, which come away clean and are not discolored, should be returned to the warm glycerin for tempering, and allowed to cool in the liquid. After cooling, the salvaged teeth should be washed with soap and water.<sup>21</sup>

At this point it may also be mentioned that a glycerin-alcohol-water solution is employed for the conservation of vulcanized rubber goods. Prinz, citing the studies of Larine, states that new rubber goods are preserved when imersed in a solution consisting of:

	%
Glycerin .....	8
Alcohol .....	8
Water, to Make .....	100

Although these studies have not been done in connection with dentures, it is interesting that industrial research workers have found that it is possible to rapidly vulcanize rubber mixtures in glycerin under pressure at high temperatures under accurately controlled conditions.<sup>33</sup> Comparative studies have shown that this method of vulcanizing in glycerin is as good or better than other curing processes.<sup>34</sup> This may have applications in prosthetic dentistry.

Somewhat in the same order of application is a new and important use for glycerin recently indicated by Kelly<sup>35</sup> in an article on synthetic plastics in surgical denture splints. This report discussed the advantages and technic of using tooth-colored plastics from acrylic resins in denture splints designed from immediate restoration service. Kelly has found that plastic applications of this type are practical and will fulfill the requirements of any transitional denture. During the detailed technic presentation, in the step for processing the case, Kelly states that, "In this technique glycerin is preferred to boiling water or the vulcanizer.

This is because the technician may see just what is going on at all times; also, the temperature may be raised high enough to insure a complete polymerization of the product." Essential information concerning this glycerin treatment is also given.

Modern glycerin-containing resins, known as glycerin-phthalate, alkyd or glyptal resins have also been used for denture purposes. Speaking of the advantages of these glycerin-containing resins, Moore<sup>36</sup> states that, "In many respects this material has the nearest to the ideal properties, its color, color life, and translucency are practically perfect. It has a strength about the same as the cellulose compounds, and its absorptive properties are very good if the material is properly cured." However, the process of constructing a glyptal resin denture is rather time-consuming.

A process for making artificial dentures from a glycerin-containing resin has been patented.<sup>37</sup>

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## PHARMACEUTICALS

GLYCERIN IS a basic, essential material in pharmacy. Changes made in official glycerin-containing preparations were recognized as but temporary expedients and were stated as such. No fully satisfactory substitute for glycerin has been found. Developments in pharmacy continue to utilize glycerin in many new ways.

Glycerin is used in many pharmaceutical preparations, because it offers good physical characteristics. These have been reviewed by several authorities. Merrill<sup>1</sup> for example, listed some of the important uses for glycerin as follows: (a) humectant, (b) vehicle, (c) solvent, (d) sweetening agent, (e) emollient, (f) reactive material, (g) lubricant, (h) softening agent, (i) penetrant, and (j) anti-freeze agent. To this might well be added the observations made by Prinz<sup>2</sup> in Canada. This authority pointed out that among the several functions of glycerin in pharmaceutical preparations, the following are among the most important: (a) to give a certain "body" or viscosity to liquid preparations, (b) to prevent enzymic decomposition, particularly fermentation, of liquid preparations, (c) to act as a solvent for certain drugs; and, (d) to prevent the drying out of ointments, creams and pastes made with water.

In any discussion of its properties, one cannot omit the fact that glycerin, unlike many other solvents, is safe to use both in oral preparations and those intended for external, topical application. Indeed the importance of this characteristic was made quite evident when it became necessary for the government<sup>3</sup> as well as other interested groups,<sup>4</sup> to issue warnings against the dangers of materials suggested as glycerin substitutes. These groups stressed the necessity for thorough investigation of all suggested glycerin substitutes. Some substances which may have served in certain instances are far too toxic for medicinal use.<sup>3, 4</sup> British

studies <sup>5</sup> have shown that the mucilage type of glycerin substitutes possesses none of the water-holding properties peculiar to glycerin and other hygroscopic materials. In his discussion of the subject, Prinz<sup>2</sup> reported that, as a solvent, glycerin is difficult to replace and he warned that it would be wise to reserve some glycerin for such cases where no other solvent would serve. Speaking as a cosmetician, de Navarre<sup>6</sup> pointed out that spreading and plasticizing properties of glycerin would be most difficult to replace. The spreading effect, he noted, is particularly noticeable in vanishing creams which roll unless there is a sufficient amount of glycerin present. This fact becomes quite pertinent when it is realized that vanishing cream bases (e.g., "washable," greaseless ointment bases) are finding ever-widening utility in topical medication for the treatment of dermatological conditions, infections, wounds and burns.

The role played by glycerin is evident from the recent report of the Council on Pharmacy and Chemistry of the American Medical Association<sup>7</sup> on the local use of sulfonamide compounds in dermatology. The following quotation from this report is quite indicative: "What type of vehicle should be used for exhibiting these compounds? Unfortunately the sulfonamides are hardly soluble in water, much more so in glycerin, and Lain notably employs sulfanilamide in such a supersaturated solution on gauze, claiming excellent results. Kalz and Prinz have used a glycerin emulsion for their work. It has been clearly brought out by Pillsbury, Livingood and his co-workers, Prinz and Kalz, and others that greasy bases are unsatisfactory for applying sulfonamide locally. A grease will seal off the area, it does not mix with serum, and it may coat over the underlying infection and furnish an anaerobic pocket in which the infection may thrive. Moreover, bacteria covered with a film of grease will not be so easily reached by the medicament. Oil-in-water emulsion bases provide a more satisfactory medium than vanishing cream compounds and are apparently the best bases for applying any of the sulfonamides.

The glycerin-containing oil-in-water emulsion type base, developed by Pillsbury and his collaborators,<sup>8</sup> used as an example in the A.M.A. report, is as follows:

	%
Sulfathiazole .....	5.0
Sodium Lauryl Sulfate .....	1.0
Stearyl Alcohol .....	10.0
Cetyl Alcohol .....	3.0
Spermaceti .....	10.0
Glycerin .....	61.0
Water .....	61.0

However, glycerin-containing sulfonamide compositions are not limited to the treatment of dermatological conditions, but find wide application in the therapy of burns, surgical wounds, accidental wounds and other disorders. For example, in his report on the use of a preparation consisting of 30% of sulfathiazole in glycerin, Wood<sup>9</sup> found this simple combination effective in the treatment of such varied indications as: minor surgery, general surgery, leukorrhea, burns, osteomyelitis, tonsillectomy, pre-operative skin preparation, and compound fractures.

Glycerin has a well-established role in sulfonamide-containing burn-treating products. During the last year or so, so-called "sulfa films" have come into increasing use for treating burns. These compounds contain substances which on drying form protective films over the injured area. Glycerin often serves as the plasticizer for these films to keep them pliable and flexible and to prevent their drying and cracking. An example of such use is given in the report of Skinner and Waud<sup>10</sup> on a plastic film treatment of experimental burns. Two solutions were tested containing:

#### Burn Fluid 19

	Parts by Weight
Glycerin .....	80
Triethanolamine .....	5
Urea .....	5
Sulfathiazole .....	5
Sulfanilamide .....	5
Stock Solution of Methyl Cellulose .....	100
Stock Solution of Polyvinyl Alcohol .....	800

## Burn Fluid 20

	Parts by Weight
Glycerin .....	40.0
Triethanolamine .....	2.5
Urea .....	5.0
Phemerol .....	0.5
Sulfanilamide .....	5.0
Stock Solution of Polyvinyl Alcohol .....	947.0

The stock solutions of the film-forming compounds were as follows:

## Stock Solution of Methyl Cellulose

	%
Methocel 25 C.B.D. ....	8.0
Benzoic Acid .....	0.1
Ringer's Solution to .....	100.0

## Stock Solution of Polyvinyl Alcohol

	%
Polyvinyl Alcohol .....	8.0
Benzoic Acid .....	0.1
Ringer's Solution to Make .....	100.0

Studies of the results in two hundred and twenty-nine experimental burns on rabbits showed that burns treated with burn fluid 19 and 20 heal at least five days before tannic acid-treated burns, ten days before burns treated with weak triple dye solution, and a full forty days before burns treated with strong triple dye solution. These burn fluids were easily applied and gave very satisfactory eschars. Moreover, they were smooth and pliable, and being water-soluble, were readily removed after soaking for a few minutes in warm saline.

However, the usefulness of glycerin extends to most types of burn preparations including those based upon tannic acid, dyes, silver nitrate, as well as the sulfonamides.<sup>11</sup> The role of glycerin in tannic acid burn jellies, though long well-established was fully confirmed in its importance by the extensive studies of Tomski<sup>12</sup> in England. Indeed, as newer materials are adapted or suggested for burn therapy, glycerin is often concurrently advocated as an essential adjunct. Thus in a patent<sup>13</sup> covering the use of tannic acid and polyisobutylene as the two main ingredients of a creamy

emulsion for applications, it was stated that from 5 to 10% of glycerin are included as a hygroscopic and softening agent to prevent the development of a harsh or unduly stiff coating.

As a matter of fact, sterile glycerin, by itself, is finding important application in the treatment of burns, more especially burns of the hands and face where tough eschar formation is not desirable.<sup>14</sup>

Although glycerin has not been much associated with the new patent antibacterial agent, penicillin, there are indications that it may be of value too in the use of this drug. As is well known, the use of pure penicillin is limited. However, it occurred to Robinson and Wallace<sup>15</sup> that the direct application of a less pure product might be of advantage in the local treatment of wounds, furunculosis, sinus infections, gonorrhea, and other infections of the skin or mucous membranes. To produce the penicillin in contact with the lesions, they placed a gauze dressing in a Petri dish and saturated it with a medium containing 1% yeast extract, 2% dextrose, 2% cornstarch and 2% glycerin. This was sterilized in an autoclave and inoculated with penicillium.

It was found that a fair amount of penicillin was produced after four or five days and that a bacteriostatic condition would be maintained at the point of contact with the lesion. Clinical application of the penicillin dressing was made on a series of patients who had not been relieved by other forms of therapy. Results on a small series of patients were most encouraging and indicated much promise for the method.

For years glycerin has found many applications in the prophylaxis and treatment of allergic conditions. Among its most important uses is its employment as an extractive and vehicle for production of allergenic preparations used for testing or reducing sensitivity to various exciting substances.<sup>16, 17</sup> Asthma, one of the more unpleasant sequels of allergic disorders is also treated and paroxysms made less severe by the use of glycerin-containing compounds, many of them developed during the last year or so. This is especially true of new inhalants for the relief of asthmatic attacks. These inhalants, applied by means of an atomizer to provide a fine spray to afford relief of asthmatic coughing, wheezing and choking, are usually based upon the use of epinephrine (adrenalin, suprarenalin, etc.).



However, epinephrine by itself has certain undesirable effects, such as lack of stability in solution, short duration of action, irritative effects on the nose and throat, and undesired systemic side-effects. Various methods had been given to overcome these disadvantages. In 1942, Cole<sup>18</sup> advocated the use of the following glycerin-containing solution prior to an asthmatic attack:

	%
Methyl Atropine Nitrate or Bromide . . . .	0.14
Papaverine . . . . .	0.08
Sodium Nitrate . . . . .	0.08
Adrenalin . . . . .	0.05
Lactic Acid . . . . .	2.50
Glycerin . . . . .	10.00
Distilled Water, to Make . . . . .	100.00

More recently, Lockey<sup>19</sup> suggested another method for improving these inhalant sprays by the addition of glycerin. He had found that epinephrine-induced dryness of the throat will often disappear if the patient swallows a little glycerin immediately after inhaling the spray. He, therefore, prepared the following solution:

Suprarenalin Crystals . . . . .	10.0 g.
Sodium Chloride . . . . .	9.0 g.
Chlorobutanol . . . . .	5.0 g.
Sodium Bisulfite . . . . .	0.9 g.
Dilute Hydrochloric Acid . . . . .	20.0 ml.
Glycerin. . . . .	50.0 ml.
Distilled Water, to Make . . . . .	1000.0 ml.

Carefully controlled clinical tests with this preparation showed that irritation and dryness of the throat appeared 82% less frequently in the group which used the glycerized solution. Longer periods of relief were obtained also, and most patients expectorated more frequently and productively.

Back in 1941, a combination of equal parts of phenol and camphor was suggested for the treatment of "athlete's foot." Subsequent reports indicated that this mixture was dangerously caustic, especially when applied to wet surfaces. However, Verhoeff<sup>20</sup> has prepared a glycerized mixture that also contains phenol and which, it is claimed, is harmless even when applied to wet skin. The formula is as follows:

	Parts by Volume
Phenol Crystals (Melted) .....	2
Ethyl Alcohol (95%) .....	2
Glycerin .....	4

The solution is applied by thoroughly rubbing the affected region with the end of the finger; application being made twice daily, or once daily in mild cases. It is most effective immediately after the feet and lesions have been washed with soap and water. After healing, an application once a week is to be continued to prevent reinfection. Healing is rapid: about a week in mild cases, in three weeks in more severe cases. Despite the report that this composition is harmless, it is evident that any preparation with so high a proportion of phenol should be used only under a physician's direction.

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## VETERINARY MEDICINE

IF A survey of medicinal and adjunct agents used in veterinary practice were made, glycerin would rank high. Glycerin enters into such varied veterinary preparations as: antiseptics; parasiticides; healing and soothing ointments, salves and lotions; internal medicament mixtures; animal tonics, diagnostic, prophylactic and therapeutic vaccines and other biologicals; pills and capsules; laboratory reagents and others.

Glycerin is especially useful for external applications on animals for the treatment of parasitic and other infectious conditions, because it has a definite bacteriostatic action; because it is such an excellent solvent for other, more powerful antiseptics and essential drugs; because of its adhesiveness; and because, in proper concentration, it has marked soothing and emollient qualities. For example, in a discussion of "Diseases of Feeder Cattle," O'Neal<sup>1</sup> reports that a mixture of equal parts of tincture of iodine, glycerin and chloral hydrate seems to be more efficient for treating ringworm than iodine alone. In a symposium on certain external parasites in cattle, Clapp<sup>2</sup> advised to treat ringworm by scraping off the scab with a knife blade and applying tincture of iodine or a mixture of equal parts of iodine and glycerin; the mixture is also applied to the margin of the spot. In the same symposium, Culver reported that an application of iodine to the infected area, followed by the application of glycerin or a salve will effect remedy for cattle ringworm.

It has been estimated that the live stock industry in the United States annually suffers a loss amounting to \$5,000,000 through deaths to sheep from myiasis caused by infestations of blow-fly maggots. An official Canadian text on injurious parasites,<sup>3</sup> the authority for the above figures, warns that prompt measures are necessary when animals have become maggot-infested. In the case of sheep, it is advised that, "If maggots have penetrated

deeply, an application of glycerin will bring them to the surface, where they may be killed with benzol."

In Australia, where sheep raising is a major part of the nation's wealth, glycerin preparations have proven extremely effective in treating and preventing blow-fly "strike." One such preparation, which came to be known as "glycerin-diboric," because glycerin and boric acid are the chief ingredients, has been outstanding in its ability to rid the infested area of maggots and to prevent reinfection when the struck area is healing.<sup>4</sup> Tested in New South Wales,<sup>5</sup> glycerin diborate, diluted with 25% of alcohol and applied as a swab to the breech of the sheep, had a value in repelling the flies for two months during a year of light blow-fly strike. The formula for such a preparation for dressing the wounds is given<sup>6</sup> as a mixture of:

Boric Acid .....	3 lb.
Glycerin .....	1 gal.

Glycerin-containing preparations also help in cutaneous conditions of other animals. As is well known, irritable and eczematous conditions of the skin are quite common to many dogs. Ointments, of course, are unsuitable for use on oozing skin surfaces or on acutely inflamed skin. Under such circumstances, a lotion is far more preferable.<sup>7</sup> A lotion of this sort, said to be an excellent preparation for moist eczema, is an 18% solution of tannic acid in glycerin, diluted with equal, or double, its volume of water. This lotion slightly diminishes the sensibility of the nerve endings, and also has an astringent and cooling effect. Another useful lotion for controlling inflammation, and one that is at the same time antipruritic and antiparasitic, consists of:

Colloidal Calamine .....	20.0 g.
Glycerin .....	5.0 g.
Para-Chlormetacresol .....	0.1 g.
Water, to Make .....	100.0 ml.

A British formula<sup>11</sup> for a so-called "hair restorer" for dogs should be of interest:

Tincture of Cantharidin .....	2 dr.
Almond Oil .....	1 oz.
Glycerin .....	1 oz.
Lime Water, to Make .....	4 oz.

This lotion is used as a dressing for the skin, to be applied daily where the hair is thin.

Of course, many skin conditions of dogs could be prevented by the use of a suitable dog wash or shampoo, such as the following:<sup>s</sup>

Soft Soap .....	8	oz.
Glycerin .....	2½	oz.
Alcohol .....	2	oz.
Phenol .....	3	dr.
Oil of Eucalyptus .....	2	dr.
Water, to Make .....	35	oz.

Glycerin is frequently utilized in the treatment of mange. Thus, in one treatment of sarcoptic mange, where two dressings of a mixture of equal parts of oil of tar, olive oil, and oil of turpentine are applied at a three-day interval, the animals should be washed afterwards with a neutral soap and rinsed with a quart or so of warm water containing 5% of glycerin.

A general preparation for the treatment of ear mange<sup>s</sup> consists of:

	%
Cresol .....	1
Phenol or Creosote .....	1
Glycerin, to Make .....	100

Some animals, however, require more specialized preparations for this ear condition. A preparation for rabbit ear mange,<sup>9</sup> for example, can be made from:

	Parts by Weight
Mercuric Chloride .....	1
Glycerin .....	100
Ethyl Alcohol (50%) .....	200

For foxes, equal parts of tincture of iodine and glycerin has been recommended.<sup>3</sup>

A mixture advocated for treating ear trouble in dogs,<sup>8</sup> but obviously useful for other animals, can be made from:

Boric Acid .....	1	dr.
Glycerin .....	1	oz.
Phenol .....	16	gr.

To relieve irritation or pain, this combination may be used to apply to cracks in the earflaps or introduced, warm, to the inner ear.

For animal eyewashes, the soothing and other effective qualities of glycerin make it a frequent ingredient. One typical preparation of this kind, claimed <sup>7</sup> to be among the best eyewashes for irrigation and cleansing of the eye and for purulent discharges and conjunctivitis, contains:

Sodium Bicarbonate .....	15 gr.
Borax .....	15 gr.
Sodium Chloride .....	15 gr.
Glycerin .....	1 dr.
Distilled Water .....	8 oz.

Used alone, glycerin has been finding increasing employment in surgery and wound treatment,<sup>12, 10, 11</sup> and moreover, this knowledge is being applied in veterinary medicine. Kulkarni,<sup>13</sup> for example, quite recently reported that glycerin was successfully used in the treatment of a deep wound in a horse. Although, at the present stage, this work with pure glycerin is of an indicative rather than a conclusive nature, it does show that glycerin has valuable potentialities in veterinary surgery.

Glycerin-containing preparations have long maintained an established place in animal surgery and wound treatments. Devine,<sup>14</sup> for example, recently recommended a combination of:

Tincture of Iodine .....	1 dr.
Phenol .....	3 dr.
Glycerin, to Make .....	4 oz.

for cracked heels and irritations about the legs of horses. To use this preparation, a piece of cotton large enough to cover the area is saturated and covered with a sheet of cotton and bandaged on. This is to be repeated every day or two. DeVine reports that, "This is an excellent preparation for chronic scratches. We used it when horses' legs became blistered or irritated from the salt thrown on the street in cold weather. It is helpful in almost any leg irritation."

In this connection, it is interesting to note that the employment of a mixture of equal parts of glycerin and tincture of iodine is

an established procedure for the treatment of "hock-curbs" or swellings and one for which practical usage has proven excellent results.

Another winter preparation, this one for treating dogs' feet, should be of interest. Hounds' feet that have been worn and cut on crusted snow may be treated with a standard mixture of equal parts of glycerin and tannic acid. This serves to stop oozing and helps to dry the raw flesh.<sup>15</sup>

In a recent discussion on retained afterbirth, a common condition in herds where Bang's disease is prevalent, Stewart<sup>16</sup> advised that when the afterbirth has been removed and the operator's arms well washed, an application of the following solution should be used as a safeguard against infection:

Rubbing Alcohol .....	1 pt.
Glycerin .....	1 oz.
Color and Perfume .....	to suit

"The use of this wash," says Stewart, "after the operation and the aseptogen before it, will prevent the papular rash that commonly develops as a consequence of manipulation within an infected uterus."

Glycerin enters into the animal therapeutic preparations intended for oral administration. Not only is glycerin extensively employed in liquid preparations, but it is also a standard ingredient of gelatin capsules and is widely employed as a massing material for pills of all sizes and for all purposes. An example of this latter use is given in the following for making horse physic balls:<sup>8</sup>

	Parts by Weight
Barbados Aloes .....	10
Glycerin .....	1
Castor Oil .....	1
Powdered Unbleached Ginger .....	½

Syrupy medicaments, such as the following cough electuary for horses,<sup>7</sup> the dosage for which is one tablespoonful three times per day, not only utilize the suspending and solvent properties of glycerin, but also its soothing action on irritated mucous membranes:

	Parts by Weight
Powdered Camphor .....	$\frac{1}{2}$
Powdered Myrrh .....	$\frac{1}{2}$
Potassium Chlorate .....	1
Honey .....	4
Glycerin .....	4

The same solvent and soothing qualities are utilized in other animal preparations, as in the dog mouthwash <sup>7</sup> given below:

Tincture of Iron .....	1 oz.
Potassium Chlorate .....	2 oz.
Glycerin .....	4 oz.
Water, to Make .....	1 gal.

During the long winter months when sunlight is reduced and fresh forage is lacking, most animals require food, especially vitamin supplements, to maintain their health. Cod liver oil emulsions, in various strengths are now standard products to supply some of these requisites. Glycerin is used in such emulsions, as illustrated in this formula for an animal mixture: <sup>7</sup>

	Parts by Weight
Gum Arabic .....	100
Gum Tragacanth .....	100– 120
Glycerin .....	1200
Crude Cod Liver Oil .....	3700
Calcium Hypophosphite .....	50
Sodium Hypophosphite .....	50
Water .....	4000

A suitable flavoring mixture may be added if deemed necessary.

In such emulsions the role of glycerin is not merely mechanical or physical, for glycerin has definite nutritive value of its own. Glycerin readily replaces carbohydrates, having about the same caloric value.<sup>17, 18</sup>

Many phases of poultry treatment also employ glycerin. A case in point is the therapy of poultry favus as outlined by vanEs and Olney.<sup>19</sup> Since this skin disease is caused by a fungus transmitted from fowl to fowl by direct or indirect contact, the first step in treatment is isolation of the effected animals. The next step is the application of a mixture comprised of:



	Parts by Weight
Tincture of Iodine .....	1
Glycerin .....	6

This mixture should be applied two or three times per week. Even this preparation will probably not be effective when the feathered skin is involved and it appears advisable to destroy such animals rather than let them become centers of infection.

Veterinary practitioners know that medication for poultry is best given in pill or capsule form. Here again, the several properties of glycerin are brought into play, as in the following mixture to make tonic pills for fowls:<sup>8</sup>

	Parts by Weight
Ferrous Sulfate .....	2
Extract of Gentian .....	$\frac{1}{2}$
Calcium Phosphate .....	1
Glycerin of Tragacanth Sufficient to Make a Mass	

This is divided into 5-grain pills.

Somewhat similar are these tonic pills.

Ferrous Sulfate .....	1	dr.
Powdered Capsicum .....	20	gr.
Extract of Nux Vomica .....	6	gr.
Powdered Gentian .....	$\frac{1}{2}$	dr.
Glycerine of Tragacanth ....	Sufficient	Quantity

The ingredients are mixed, divided into 60 pills and coated with sugar. Each pigeon is allowed six of these pills per day.

Another form for this type of pigeon tonic is as follows:<sup>8</sup>

Ferric Oxide .....	1	oz.
Tincture of Capsicum .....	$\frac{1}{2}$	dr.
Almond Meal .....	$1\frac{1}{2}$	oz.
Glycerin .....	1	oz.

Preventive measures are as important in veterinary practice as in any other phase of modern medicine. Diagnostic and prophylactic vaccines play an essential role in these measures. It need hardly be pointed out that glycerin is frequently employed as an attenuating agent in the production of such vaccines as Pasteur anti-rabic vaccine, tuberculin-Koch, tuberculin-Denys, and others.

Other prophylactic measures similarly use glycerin, but in other ways. Animal dips, particularly sheep dips designed to destroy skin parasites, are definitely in this preventive medicine class and here again the versatility of glycerin comes into play. Typical is the following, rather old-fashioned, British "Carbolic and Glycerine Dip"<sup>8</sup> for sheep:

	Parts by Weight
Common Size .....	1
Soft Soap .....	1
Crude Glycerin .....	1
Crude Carbolic Acid .....	1

This suffices for 30 gallons of dip.

A modern sheep dip,<sup>20</sup> a compound of glycerin and arsenious oxide, can be made by simply mixing and heating until a clear syrupy liquid is obtained:

	Parts by Weight
Arsenious Oxide .....	45
Water .....	12
Glycerin (Anhydrous) .....	43

This is heated at 150°C., but if commercial glycerin, which contains varying quantities of water, is employed, the temperature should be lowered to 100°C., extending the heating time. It is claimed that this mixture is not lessened in potency by hard waters at the point of use, and that used alone, without admixture with such substances as cottonseed oil or the like, it is as effective as arsenic, sulfur and phenolic mixtures now so popular.

In the veterinary laboratory, glycerin has an essential role in the various test reagents used, it is an important ingredient of many of the staining solutions for microscopic examination and study, and is a standard mounting and preserving medium for both microscopic and macroscopic specimens. With regard to this last use, mention should be made of Mason's<sup>21</sup> discussion of methods for shipping specimens for laboratory examination. He indicated that internal animal parasites could be shipped in pure glycerin but that this fluid was particularly valuable when brains from animals suspected of rabies or equine encephalomyelitis were sent for examination. "Where a virus disease is suspected,"

Mason states, "glycerin is often desirable since it preserves the tissue, inhibits bacterial activity and viruses survive it for several days or longer."

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## CHAPTER XXVII

### OPTOMETRY

GLYCERIN UNQUESTIONABLY is a familiar material to most opticians. It is doubtful, however, that even those opticians who use this versatile fluid to speed or improve optical processes or preparations fully realize the wide potentialities of glycerin and the many varied uses to which it may be put. Thus glycerin finds employment not only in connection with abrasives, polishes and protectives for the lenses, but it also enters extensively into a host of preparations for treating and soothing the eyes.

Glycerin is used as a suspending medium for glass-grinding abrasives or polishing agents, to replace the camphor-turpentine mixture. Glycerin has body enough and is sufficiently viscous to carry the abrasive well, and in addition is water-soluble. This last property is important, for not only does it obviate the need for expensive solvents, but it is also easy to wash the abrasive away to check the work progress or to clean-up at the completion of a glass-grinding job.<sup>1</sup>

Glycerin is also utilized in the manufacture of abrasive articles required in shaping lenses for spectacles. Glycerin is employed, for example, in abrasive compositions<sup>2</sup> made with diamond particles mixed with particles of another hard mineral, as in the following example:

	Parts by Weight
Diamond Powder .....	7
Synthetic Sapphire .....	2
Alum .....	1
Clay .....	2-5
Glycerin .....	3
Glue Size .....	4

These are molded to shape and fired at 1000-1500°C. The glycerin, which volatilizes off during the heating, serves here as

a massing material to prevent drying and crumbling prior to firing.

In other instances, glycerin is added because of its plasticizing action to maintain the flexibility of abrasives in sheet form. Because of its high boiling point ( $290^{\circ}\text{C}.$ ), glycerin is still active when other, more volatile materials would ordinarily evaporate. As a rule, glycerin is added to the adhesive which bonds the abrasive particles to the backing or support materials.<sup>3, 4</sup>

During recent years, synthetic resins, made with glycerin, have been widely used as the abrasive-bonding material.<sup>5, 6, 7</sup> These alkyd glyptal glycerol-phthalate resins can be modified to meet an almost infinite variety of needs. Their employment in the manufacture of abrasive products, essential for the optical industry, is only one phase of their usefulness.

According to one patent,<sup>8</sup> owned by one of the nation's largest optical goods manufacturers, resin may be used to make polished glass articles, such as lenses, for identification. A glyptal resin or an ester gum (a combination of glycerin with a natural resin) may be employed, according to another quite recent patent,<sup>9</sup> to provide a temporary protective coating for polished glass surfaces.

Glycerin, as such, frequently enters into the formulation of many glass-marking "inks" and the like.<sup>1</sup> A typical glass-marking ink, invaluable when permanent markings are to be made on test lenses and the like, can be prepared from:

	Parts by Weight
Barium Sulfate .....	15
Ammonium Bifluoride .....	15
Ammonium Sulfate .....	10
Oxalic Acid .....	8
Glycerin .....	40
Water .....	12

If this preparation is too thick, more water is added; the action may be speeded by adding up to 5% of sodium fluoride. It must be used in a hood or a well-ventilated room. The glass should be clean and warmed slightly before writing on it with this fluid; it is allowed to act on the glass for about 2 minutes.

Where it is desired to merely affix a suitable label to glass surfaces, the following glycerin-containing mucilage<sup>10</sup> will prove most effective:

Tragacanth .....	1 oz.
Acacia .....	4 oz.
Thymol .....	14 gr.
Glycerin .....	4 oz.
Water, to Make .....	2 pt.

The gums are dissolved in 1 pint of water, strained, and the glycerin is added in which the thymol has been mixed, the mixture is well shaken and enough water is added to make 2 pints. The mucilage should be shaken before use.

No pair of spectacles, no matter how carefully prescribed and prepared, is of much value if covered with dust and grime. Hence, the importance to the prescribing optician to have simple spectacle cleaning preparations available for his own and dispensing use. One of the simplest of such products <sup>11</sup> consists of:

	Parts by Weight
Alcohol .....	45
Glycerin .....	10
Water .....	45

This may be colored if desired.

The presence of glycerin in such spectacle cleaners serves a double purpose; not only does it help to clean the lenses, but the thin film of glycerin left on the glass helps to prevent misting and fogging from temperature changes in the winter and from perspiration in the summer. A paste preparation <sup>12</sup> that embodies both of these properties to a high degree consists of:

	Parts by Weight
Soap .....	70
Glycerin, C.P. ....	30

Soaps with fillers should be avoided. A soap with a coconut oil base is considered quite satisfactory. The amount of glycerin to be used will vary with the different soaps and with their water content. To use, apply a small amount of the paste to a soft cloth and rub on both sides of the spectacles; then polish until thoroughly dry.

Polishing cloths, <sup>11</sup> with similar uses, can be made from:

Water .....	5 qt.
Glycerin .....	1 oz.
Sodium Oleate .....	1 oz.

These are boiled together for 5 minutes, then a cloth is immersed (usually flannel) into the boiling solution for 10 minutes.

Opticians who serve industrial areas are frequently called upon to prescribe suitable eye protecting devices, such as goggles. One difficulty about goggles is that perspiration causes fogging and clouding, rendering them useless. According to a report by Culler<sup>13</sup> on visual efficiency in industry: "Perspiration fogging the glasses can be relieved to some extent by sweatbands, glycerin pencils or specially prepared soaps."

Glycerin pencils<sup>14</sup> to meet the above requisite can be prepared from:

Glycerin .....	325 ml.
Sodium Hydroxide (Sticks) .....	50 g.
Stearic Acid .....	625 g.

The glycerin is heated to the boiling point and the sodium hydroxide is dissolved in it. The stearic acid is melted in a separate vessel, and added to the glycerin mixture with constant stirring. When the action ceases, the mass is poured into molds.

This quantity of mixture will make about 500 glycerin pencils and it is said to have been found satisfactory for use on goggles during both winter and summer.

In passing, it may be said that glycerin-containing preparations have been used as laminating materials for manufacturing safety glass such as is used in making shatter-resistant goggles.<sup>15, 16</sup>

In suitable dilution, glycerin has a soothing effect on delicate membranes, it is frequently employed in soothing eye lotions for general use, and medicated eye preparations for special application. One preparation, frequently prescribed as an excellent eye wash to take the place of boric acid solution and said to have greater comforting and cleansing effects,<sup>17</sup> is the following:

Sodium Bicarbonate .....	15 gr.
Sodium Biborate .....	15 gr.
Sodium Chloride .....	15 gr.
Glycerin .....	1 dr.
Distilled Water .....	8 oz.

This solution, it is reported, is often preferred to boric acid solution and it will be found very useful for general and free use in the various forms of conjunctivitis. It is exceptionally valuable

for washing out the eyes following exposure to the wind and dust after motoring, hiking, and the like.

On the same order and with similar uses, is the following simple eye lotion: <sup>18</sup>

	Parts by Weight
Boric Acid .....	25
Sodium Borate .....	30
Glycerin .....	10
Witch Hazel Water .....	50
Distilled Water, to Make .....	1000

When an astringent eye lotion is required, a preparation containing the following, given by the same authority,<sup>18</sup> will serve:

	Parts by Weight
Zinc Sulfate .....	0.5
Sodium Borate .....	32.0
Boric Acid .....	16.0
Glycerin .....	50.0
Peppermint Water .....	75.0
Rose Water .....	150.0
Camphor Water .....	150.0
Distilled Water, to Make .....	1000.0

The sulfate is dissolved in the peppermint water, the borate and boric acid in the glycerin and rose water and the ingredients are mixed. Then the camphor water is added and the eye lotion is made to the desired volume with distilled water.

The formulas for many other glycerin-containing eye lotions with general and with specific applications could be given, but the above are indicative. It should be remembered, however, that all eye preparations must be made with the purest chemicals and sterile distilled water, filtered clear and dispensed in sterile bottles. If the ingredients are thermostable, sterilization by autoclaving is recommended. If this is not practicable, filtration-sterilization is advocated.

When discussing the use of preservatives in these eye preparations, Holland<sup>18</sup> makes this pertinent observation: "If the collyrium is to be diluted before using, glycerin is sometimes used as a suitable preservative. In eye lotions, not more than 6% to 8% of glycerin is advisable, though up to 25% is necessary for certainty in preservation. Some workers make up the collyria and



label it double strength, and use from 12 to 16% of glycerin. In the latter percentages, the glycerin greatly decreases the tendency for fungus growths to appear."

In this brief review, some of the many varied, direct and indirect uses of glycerin in optical practice have been indicated. Many more such applications are well known. However, it is evident that glycerin is a most useful aid to the prescribing optician.

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## GLYCERIN DERIVATIVES

*H. Bennett*

COMMERCIAL PRODUCTION of partial † glycerol ‡ esters has been increasing steadily in volume. These are used principally because of their emulsifying and penetrating (surface-active) properties. They are referred to technically as non-ionic surface-active agents.

Non-ionic surface-active agents, as their name implies, are not ionizable and owe their effectiveness to a proper balance between certain hydrophilic (polar) and lyophilic (non-polar) groups in their molecules. The hydrophilic character is usually obtained by the presence of a certain minimum of accumulated polar groups, such as free hydroxyl or ether-oxygen groups.

TABLE I

Properties of Some "Non-Dispersible" Non-Ionic Surface Active Agents \*

Compound	Form	Melting Point °C.	Miscibility* with—				
			Ethanol	Acetone	Toluene	Naph- tha	Mineral Oil
Glycerol							
Monolaurate	Semi-Solid	22-23	M	M	M	M	M
Monooleate	Semi-Liquid	38	M	M	PM	PM	PM
Monoricinoleate	Liquid	....	M	M	PM	I	I
Monostearate	Solid	55-57	MH	MHX	MH	MH	MH

\* Abbreviations: M—miscible; P—partly; X—in limited proportions; I—immiscible; H—hot. Miscibility in the case of solids refers to the melted material.

The stability of non-ionic surface-active agents toward salt solutions, hard water, earth alkali or heavy metal salt solutions is usually far greater than that of cationic or anionic agents of a similar degree of water solubility. Some of them are not affected,

† By partial glycerol ester is meant a mono or diglyceryl ester of a higher fatty acid, e.g., glyceryl monostearate.

‡ Glycerol is the designation for glycerin, preferred by chemists.

## *Glycerin Derivatives*

or only little affected, by limited contact with strong acids ~~and~~ alkalis. They are neutral, but may be adjusted to give an alkaline or acidic reaction without necessarily losing their usefulness. They may be used in conjunction with either the cationic or anionic surface-active agents, and such combinations usually have greater effectiveness than either of the ingredients alone. For instance, blends of polyhydric alcohol esters with soaps are well-known as effective emulsifiers.

The non-ionic surface-active agents are superior to the anionic and cationic agents in range of compatibility with solvents and chemicals. Their effectiveness may be further improved by the addition of certain solvents, such as alcohols, glycols, or glycol-ethers, terpene alcohols or fatty acids. Their adsorption by wool and possibly by other fibers is less than that of anionic or cationic compounds. They usually will not react with weak organic acids or bases used in conjunction with them, such as certain dyes or pharmaceuticals.

The non-ionic surface-active agents may be roughly divided into three classes, according to their behavior with water. There are those that do not, or only poorly, disperse in water, but may have the property of imbibing a quantity of it. We shall refer to them as non-dispersible. The second group will disperse when stirred or shaken with water. Some of the compounds in this group are able to absorb considerable quantities of water without turning cloudy. We shall call these agents dispersible. The last group is water-soluble, the solutions formed being clear, or opalescent, like those of soap.

There are no distinct boundaries between these groups, and compounds of each type may be obtained by various combinations of chemicals. Small admixtures of alcoholic solvents or fatty acids can shift their solubility properties considerably; sometimes a material will dissolve clearly in high concentration, but yield a milky dispersion on greater dilution; sometimes the presence of electrolytes will diminish the water solubility of these surface-active agents.

The non-ionic surface-active agents of the non-dispersible type have already found numerous uses. Although they resemble oils greatly, they have a much lower surface tension and will effectively lower the surface tension of oils in which they are dissolved.

Some of them have been found to form water-in-oil emulsions and help to stabilize them, such as in shortenings or in margarine, and to improve the baking qualities of certain types of pastry. Some have a distinct wetting effect upon pigments in oil or solvent media, facilitating grinding, dispersion or suspension.

All of them act as strong assistant emulsifiers and improve the action of small amounts of soap, fatty alcohol sulfates, aryl sulfonates, and similar compounds.

They are often of value as lubricants, plasticizers and softeners; they serve as mutual solvents for polar and non-polar compounds like soap and mineral oils, or for soap, alcohol or water, and vegetable oils, and as solvents for sterols, phosphatides, dyes, or pharmaceuticals. They have been found to act as pour-point depressants for lubricating oils, as crystallization inhibitors for certain vegetable oils, as stabilizers for anti-detonant solids suspended in fuels, as dispersing agents for peanut solids in peanut butter and for cocoa in chocolate fat, as solvents for metallic soaps, as water-absorbent bases for suppositories, and in preparing specimens for the microtome. They are useful stabilizers for quick-breaking insecticidal spray emulsions. In general, they are most useful where action on a non-aqueous medium is more important than that on an aqueous one.

The water-soluble group of the non-ionic surface-active agents resembles the dispersible type, but it is no longer easily compatible with all non-polar solvents. Aqueous solutions of these compounds are opalescent or even completely clear. In this group are found compounds capable of good wetting and penetrating action, particularly for aqueous solutions of electrolytes and metallic salts. Some of the compounds are emulsifiers and dispersing agents useful under special conditions, such as high electrolyte concentration. Many also have a frothing action. There are certain emulsions which will not stand up if stabilized by compounds of the dispersible type alone, but are stable when a compound of the water-soluble type is added. Many of them will improve the stability and action of other wetting agents.

Examples of this type of compound are certain partial esters of highly polymerized glycerol and of hydroxyalkyl ethers of glycerol.

**Glyceryl Laurate S \***

(Glyceryl Monolaurate)

## Physical Properties

Color and Form	Cream, Semi-Solid
Odor	Very Faint
Melting Point	24–25°C.
pH (5% Aqueous Dispersion at 25°C.)	8.5–8.7
Specific Gravity (25/25°C.)	0.980

Glyceryl laurate S is completely soluble in alcohol, hydrocarbons, mineral and vegetable oils and is dispersible in water.

It can be used as an anti-foaming agent, e.g., for the reduction of foam for casein and similar proteins used in edible products. It is also used as a dry-cleaning soap base. It dissolves quickly and clearly in all dry-cleaning solvents, possesses high detergent value, acts as a solvent for grease and helps emulsify and remove water-soluble dirt.

Glyceryl laurate S is an ester of C.P. glycerin and lauric acid obtained from edible coconut oil and can, therefore, be considered non-toxic. It is very suitable as an emulsifying agent for the manufacture of fluid, edible, and pharmaceutical oil emulsions. It is also of interest as a smoothing and dispersing agent, particularly for proteins and similar products.

**Glyceryl Monoricinoleate S**

(Glycerol Monoricinoleate)

## Physical Properties

Color and Form	Amber Fluid
Odor	Faint
pH (5% Aqueous Dispersion at 25°C.)	9.0–9.1
Specific Gravity (25/25°C.)	1.020

Glyceryl monoricinoleate is completely soluble in alcohol and vegetable oils, insoluble in hydrocarbons and mineral oils, and dispersible in water.

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\*The glycerin derivatives that follow are being produced on a semi-commercial scale.

For the manufacture of cosmetic emulsions, particularly for hair pomades, brilliantines, etc., glyceryl monoricinoleate S replaces sulfonated castor oil and has the advantage that it does not turn rancid or thicken with age. Being completely water-dispersible, it is readily removed by water. It is a good solvent for oil-soluble dyes. Because of its emulsifying properties, it enables oil-soluble dyes to be dispersed in water.

Glyceryl monoricinoleate S, being only slightly hygroscopic, non-volatile and non-drying, replaces glycerin in the manufacture of stamp pad and similar inks.

## Glyceryl Monostearate S

(Glyceryl Monostearate)

### Physical Properties

Color and Form	Tan, Wax-Like Solid
Odor	Faint
Melting Point	56–57°C. (Capillary Tube)
pH (3% Aqueous Dispersion at 25°C.)	9.3–9.7
Specific Gravity (25/20°C.)	0.970

Glyceryl Monostearate S is completely soluble in hot alcohol, hot hydrocarbons, hot mineral oils, and hot vegetable oils. It is dispersible in hot water.

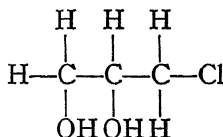
It is used for edible, pharmaceutical, and cosmetic emulsions as an emulsifying agent, e.g., for paste emulsions of edible oils, for the manufacture of greaseless creams, etc.

Glyceryl monostearate gives a good protective coating for hygroscopic powders and similar products. Edible powders, crystals, and tablets which absorb moisture from the air have a tendency to lump, cake and decompose on standing. A solution of glyceryl monostearate S in hot alcohol or other suitable solvent is sprayed on the powder which can be tumbled in a heated barrel until all the solvent has evaporated. This leaves the product coated with a thin, protective film which is dispersed and does not prevent dissolving of the product when it is thrown into water.

Glyceryl monostearate S is also used as a small addition to oils, fats and shortenings for improving their smoothness and whiteness.

Glyceryl  $\alpha$ -Monochlorohydrin

The structural formula of glyceryl  $\alpha$ -monochlorohydrin is:



## Physical Properties

Molecular Weight	110.52
Boiling Range (ASTM Gasoline Still)	90% between 136 and 142°C., at 40 mm.
Specific Gravity (25/25°C.)	1.32
Weight per Gallon	11.0 lb.
Refractive Index ( $n_D^{25}$ )	1.4781

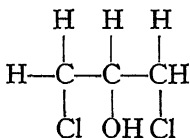
Glyceryl  $\alpha$ -monochlorohydrin is completely soluble in water, alcohol, and glycerin, but it is insoluble in carbon tetrachloride, benzene, gasoline.

It also dissolves readily in cellulose acetate and is miscible with nitrocellulose in butyl acetate solution. It is not a solvent for ester gum, rosin, damar gum, carnauba wax, and does not mix with linseed oil.

Glycerin  $\alpha$ -monochlorohydrin is the starting point for many syntheses, such as those of the glycerin ethers, amines, and other glycerin derivatives. It has unique solvent powers due to the combination of hydroxyl and chloride groups in its molecule and it merits consideration as a selective solvent. It has been suggested as a poison for rodents.

Glyceryl  $\alpha$ ,  $\gamma$ -Dichlorohydrin

The structural formula of glyceryl  $\alpha$ ,  $\gamma$ -dichlorohydrin is:



## Physical Properties

Molecular Weight	128.97
Boiling Range (ASTM Gasoline Still)	90% between 172 and 178°C., at 736 mm.
Specific Gravity (25/25°C.)	1.359
Weight per Gallon	11.33 lb.
Refractive Index ( $n_D^{25}$ )	1.479

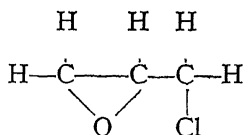
Glyceryl  $\alpha$ ,  $\gamma$ -dichlorohydrin is completely soluble in alcohol, glycerin, carbon tetrachloride, benzene and only slightly soluble in water and gasoline.

It is a good solvent for ester gum, rosin, cellulose acetate, and it is miscible with linseed oil and cellulose nitrate in butyl acetate, but it does not dissolve damar gum or carnauba wax.

Glycerin  $\alpha$ ,  $\gamma$ -dichlorohydrin is the starting point for the synthesis of the glyceryl esters, amines, and epichlorohydrin. Its solubility in most organic solvents as well as its solvent powers for a wide variety of compounds make it valuable for many applications in the solvent field.

## Epichlorohydrin

The structural formula of epichlorohydrin is:



## Physical Properties

Molecular Weight	92.50
Boiling Range (ASTM Gasoline Still)	90% between 114 and 118°C., at 736 mm.
Specific Gravity (25/25°C.)	1.18
Weight per Gallon	9.83 lb.
Refractive Index ( $n_D^{25}$ )	1.439

Epichlorohydrin is soluble in alcohol, carbon tetrachloride, benzene, gasoline, linseed oil, but it is insoluble in glycerin and water.

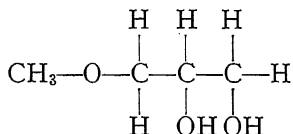
It dissolves readily ester gum, rosin, cellulose acetate, and is miscible with cellulose nitrate in butyl acetate.



Its oxide ring makes epichlorohydrin a very reactive compound and it is useful in many syntheses. Its solvent powers especially recommend it for lacquer formulation. It is useful for inhibiting mold growth.

### Glyceryl $\alpha$ -Monomethyl Ether

The structural formula of glyceryl  $\alpha$ -monomethyl ether is:



### Physical Properties

Molecular Weight	106.08
Boiling Range (ASTM Gasoline Still)	90% between 215 and 220°C., at 745 mm.
Specific Gravity (25/25°C.)	1.114
Weight per Gallon	9.29 lb.
Refractive Index ( $n_D^{25^\circ}$ )	1.442

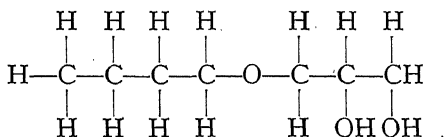
Glyceryl  $\alpha$ -monomethyl ether is soluble in water, alcohol, glycerin, benzene. It is insoluble in carbon tetrachloride and gasoline.

It is a good solvent for rosin and is compatible with nitrocellulose in butyl acetate.

Glyceryl  $\alpha$ -monomethyl ether may be used for the manufacture of alkyd resins. Its two free hydroxyl groups suggest the possibility of using it in syntheses for the preparation of compounds having more than one type of functional group. Its solubility characteristics recommend it for use as a selective solvent.

### Glyceryl $\alpha$ -Mono-n-Butyl Ether

The structural formula of glyceryl  $\alpha$ -mono-n-butyl ether is:



## Physical Properties

Molecular Weight	148.2
Boiling Range (ASTM Gasoline Still)	90% between 133 and 137°C., at 18 mm.
Specific Gravity (25/25°C.)	1.00
Weight per Gallon	8.33 lb.
Refractive Index ( $n_D^{25}$ )	1.434

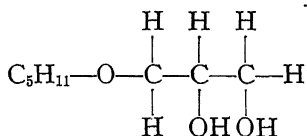
Glyceryl  $\alpha$ -mono-*n*-butyl ether is soluble in alcohol, carbon tetrachloride, benzene, gasoline, linseed oil, but is only slightly soluble in water and glycerin.

It readily dissolves ester gum and rosin. It may be used as a solvent and for the preparation of alkyd resins and ether-esters.

Glyceryl  $\alpha$ -Monoisoamyl Ether

This compound is prepared from isoamyl alcohol derived from pentane and may, therefore, contain small amounts of other amyl isomers.

The structural formula of glyceryl  $\alpha$ -monoisoamyl ether is:



## Physical Properties

Molecular Weight	162.14
Boiling Range (ASTM Gasoline Still)	90% between 252 and 260°C., at 745 mm.
Specific Gravity (25/25°C.)	0.987
Weight per Gallon	8.22 lb.
Refractive Index ( $n_D^{25}$ )	1.442

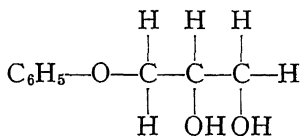
Glyceryl  $\alpha$ -monoisoamyl ether is soluble in water,\* alcohol, glycerin,\* carbon tetrachloride, benzene, linseed oil and gasoline.

It is a good solvent for rosin and is miscible with nitrocellulose in butyl acetate. It is useful in the preparation of alkyd resins and in the synthesis of ether-esters. It can also be used for solvent purposes.

\* In certain proportions only.

### Glyceryl $\alpha$ -Monophenyl Ether

The structural formula of this compound is:



#### Physical Properties

Molecular Weight	168.10
Color and Form	White Crystalline Solid
Melting Point	53–54°C.
Boiling Point	150–155°C., at 4 mm.

Glyceryl  $\alpha$ -monophenyl ether is soluble in water, alcohol, glycerin, carbon tetrachloride, (60°C.), and benzene; it is insoluble in gasoline and carbon tetrachloride (25°C.).

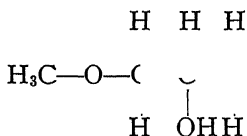
It is a good solvent for ester gum, rosin, and cellulose acetate, and is compatible with nitrocellulose in butyl acetate.

Glyceryl  $\alpha$ -monophenyl ether may be used in the production of special types of alkyd resins. Its two free hydroxyl groups offer possibilities for synthesis of compounds containing additional functional groups.

Because of its compatibility with cellulose esters and its high boiling point, it is suggested for use as a plasticizer in products containing these substances.

### Glyceryl $\alpha$ , $\gamma$ -Dimethyl Ether

The structural formula of this compound is:



#### Physical Properties

Molecular Weight	120.15
Boiling Range (ASTM Gasoline Still)	90% between 164 and 170°C., at 736 mm.
Specific Gravity	(25/25°C.) 1.01
Weight per Gallon	8.42 lb.

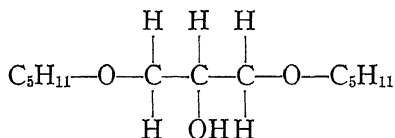
Glyceryl  $\alpha$ ,  $\gamma$ -dimethyl ether is soluble in water, alcohol, glycerin, carbon tetrachloride, gasoline, benzene, but it is insoluble in linseed oil.

It is a good solvent for rosin and cellulose acetate, and it is miscible with cellulose nitrate in butyl acetate. It has manifold uses as a solvent and plasticizer.

### Glyceryl $\alpha$ , $\gamma$ -Diisoamyl Ether

This compound is prepared from isoamyl alcohol derived from pentane and may, therefore, contain small amounts of other amyl isomers.

The structural formula of glyceryl  $\alpha$ ,  $\gamma$ -diisoamyl ether is:



#### Physical Properties

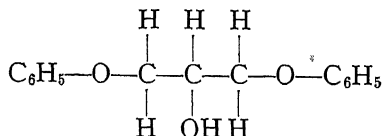
Molecular Weight	232.35
Boiling Range (ASTM Gasoline Still)	90% between 147 and 153°C., at 10 mm.
Specific Gravity (25/25°C.)	0.92
Weight per Gallon	7.66 lb.
Refractive Index ( $n_D^{25}$ )	1.432

Glyceryl  $\alpha$ ,  $\gamma$ -diisoamyl ether is soluble in alcohol, carbon tetrachloride, benzene, gasoline, and linseed oil, but it is insoluble in water and glycerin.

It readily dissolves ester gum and rosin, and can be used as a solvent and plasticizer.

### Glyceryl $\alpha$ , $\gamma$ -Diphenyl Ether

The structural formula for this compound is:



## Physical Properties

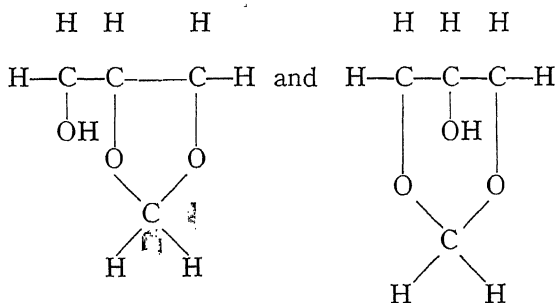
Molecular Weight	244.28
Color and Form	White Crystalline Solid
Melting Point	80–81°C.

Glyceryl  $\alpha$ ,  $\gamma$ -diphenyl ether is soluble in alcohol, benzene, and linseed oil. It is insoluble in water, glycerin, carbon tetrachloride, and gasoline.

It acts as a good solvent for ester gum, rosin, carnauba wax, and cellulose acetate, and is compatible with cellulose nitrate in butyl acetate. It is used as a plasticizer.

## Glycerin Formal

This compound is a mixture of the following isomers:



## Physical Properties

Molecular Weight	104.06
Boiling Range (ASTM Gasoline Still)	90% between 192 and 195° C., at 738 mm.
Specific Gravity (25/25° C.)	1.22
Weight per Gallon	10.13 lb.
Refractive Index ( $n_D^{25}$ )	1.436

Glycerin formal is soluble in water, alcohol, glycerin, carbon tetrachloride, and benzene, but it is insoluble in gasoline.

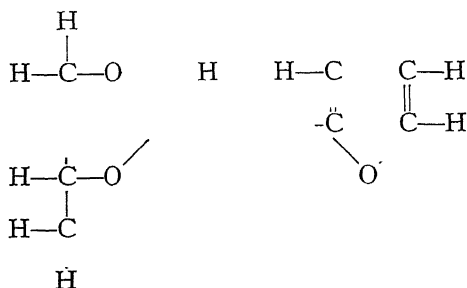
It is a good solvent for ester gum, rosin, cellulose, acetate and is miscible with cellulose nitrate in butyl acetate.

This compound can be used as a high-boiling solvent for lacquers. Due to a very slow decomposition to formaldehyde and

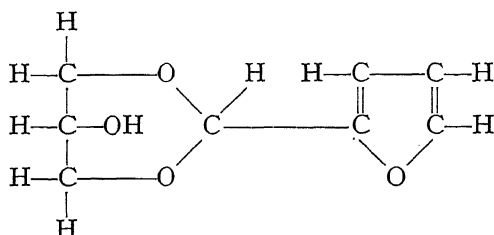
glycerin, in the presence of water, glycerin formal may be useful as a preservative against molds and bacteria.

### Glycerin Furfural

This compound is a mixture of the following isomers:



and



### Physical Properties

Molecular Weight	170.16
Boiling Range (ASTM Gasoline Still)	90% between 163 and 167°C., at 22 mm.
Specific Gravity	(25/25°C.) 1.27
Weight per Gallon	10.6 lb.

Glycerin furfural is soluble in alcohol, insoluble in gasoline, carbon tetrachloride and has a limited solubility in water, glycerin, benzene.

It readily dissolves rosin, cellulose acetate, and is compatible with cellulose nitrate in butyl acetate.

Glyceryl furfural is suggested as a high-boiling solvent for use in lacquers. It may also be useful as a preservative against molds and bacteria as, in the presence of water, it slowly decomposes to furfural and glycerin.

## LIST OF GLYCERIN USES

THE FOLLOWING list covers the processes and compositions in which glycerin is an ingredient. It is based not only upon the more widely known and established uses but also upon specialized applications shown by the technical, patent, and research literature. A single heading may refer to one use or, more generally, may signify many, often scores, of modifications, processes or uses under a single category.

The first half of the list relates to glycerin uses in the material arts and sciences and the second half to what may be termed "human" uses, that is, medicines and foods for both internal consumption and external application as well as wrappings for food and cosmetics which for the same reasons must be absolutely free from any toxic ingredient.

### Air Conditioning and Refrigeration

- 1 Air drying medium
- 2 Component of certain types of coolants
- 3 Flange packings
- 4 Gas conduit liners (sealing and dust laying)
- 5 Gasket pastes
- 6 Gas sealing compositions (glue-glycerin)
- 7 Insulating cork compositions
- 8 Joint sealing compositions (e.g., glycerin-litharge)
- 9 Oil and gas-resistant lubricants
- 10 Oilproof gaskets

- 11 Preventing precipitation in calcium chloride brines
- 12 Refrigerant-non-corrosive and non-evaporating
- 13 Thermostatic regulator bulbs

### ALKYDS

- 14 Protective coatings
- 15 "Stop-leak" preparations in circulating systems

### Adhesives and Pastes

- 16 Adhesion-preventing compositions
- 17 Adhesives for glass, tin and lithographed surfaces

- |   |  |
|---|--|
| 18 Adhesives for textiles,<br>leather, paper, etc.                              | 42 Automobile polishes and<br>cleaners   |
| 19 Bookbinding adhesives  | 43 Brake fluids  |
| 20 Container-sealing adhe-<br>sives   | 44 Brake linings and clutch<br>facings   |
| 21 Enameled and plated sur-<br>faces  | 45 Gaskets and washers   |
| 22 Envelope adhesives   | 46 Glass anti-mists and anti-<br>fog compositions                                |
| 23 Gas- and oil-leak sealing<br>compositions                                    | 47 Glass polishes  |
| 24 General plasticizer for<br>adhesives   | 48 Leather treatments and<br>cleaners  |
| 25 Gummed tapes   | 49 Lubricants for rubber<br>shackles   |
| 26 Label adhesives  | 50 Metal treatments (e.g.,<br>ball bearings, etc.)                               |
| 27 Laminating adhesives for<br>wood, paper, cloth, etc.                         | 51 Reinforcing inner tubes<br>for tires  |
| 28 Library, photographic,<br>etc., pastes                                       | 52 Safety glass (plasticizer<br>for laminant)                                    |
| 29 Mucilages  | 53 Sealing compositions for<br>radiator leaks)                                   |
| 30 Pad adhesives  | 54 Shock absorber fluids   |
| 31 Postage stamp adhesives  | 55 Solvent for "antiknock"<br>chemicals for automo-<br>bile fuels and lubricants |
| 32 Restoring glue and main-<br>taining its flexibility                          | 56 Special lubricants  |
| 33 Rubber-casein adhesives  | 57 Tire-healing compositions   |
| 34 Self-sealing adhesives<br>(e.g., "Scotch" tape)                              | 58 Tire-preserving paints  |
| 35 Silicate adhesives   | 59 Tire manufacture  |
| ALKYDS  | 60 Valve grinding composi-<br>tions  |
| 36 Bonding agents for<br>pressed cork boards                                    | 61 Waterproofing composi-<br>tions for hoods, etc.                               |
| 37 Heat-sealing adhesives   | ALKYDS   |
| 38 Laminating   | 62 Artificial leather uphol-<br>stery  |
| 39 Laminating cellulose foil,<br>metal foil, etc., to paper,<br>cardboard, etc. | 63 Brake linings   |
| <b>Automotive</b>   | 64 Gaskets   |
| 40 Antifreeze solutions   | 65 Primers for nitrocellulose<br>coatings  |
| 41 Antistatic fan belt treat-<br>ments  | 66 Protective finishes<br>(paints)   |



**Cements**

- 67 Cement coloring compositions
- 68 Gelatin cements
- 69 Glycerin-litharge cements  
for numerous bonding  
and repair uses
- 70 Glycerin-litharge mortars
- 71 Linoleum and tile cements
- 72 Oilproof and waterproof  
binders
- 73 Stain-removing preparations  
(iron, coffee, etc.)
- 74 Tool handle cement
- 91 Polishing compounds for  
lacquered surfaces
- 92 Rug and carpet cleaners
- 93 Special detergents
- 94 Stain removers (mustard,  
lipstick, coffee, etc.)
- 95 Stove polishes
- 96 Straw hat cleaners
- 97 Upholstery cleaners
- 98 Watch cleaner solutions

**Cleaners and Laundry Aids**

- 75 Automobile cleaners and  
polishes
- 76 Automobile polishes
- 77 Benzin cleaning jellies
- 78 Celluloid window cleaner
- 79 Cleaning cloths and pads
- 80 Component of transparent  
soaps, toilet soaps, etc.
- 81 Detergency testing mixture
- 82 Fabric marking inks
- 83 Furniture polishes
- 84 General household cleaning  
mixtures
- 85 Glass cleaners and  
polishes
- 86 Gloss starches
- 87 Glycerin derivatives in
  - 1) Detergents
  - 2) Wetting agents
  - 3) Dispersing agents
- 88 Leather polishes and  
cleaners
- 89 Masonry cleaners
- 90 Metal polishes
- 99 Anodizing aluminum  
(Alumilite, Tennent's  
and other processes)
- 100 Antistatic dressings and  
treatments
- 101 Battery electrolytes
- 102 Carbon electrode treatments
- 103 Coloring electric bulbs
- 104 Cleaning etched electrodes
- 105 Conductive inks (with  
graphite)
- 106 Discharge devices
- 107 Electric bulb identifying  
inks (for interior of  
bulb)
- 108 Electrolytic condensers
- 109 Electrolytic production of  
iron powder
- 110 Electroplating of metals  
(nickel, iron, cadmium,  
tungsten, zinc)
- 111 Electroplating resists or  
stops
- 112 Electropolishing of metals  
(nickel, iron, German  
silver, stainless steel)
- 113 Enamels for electrical  
resistors

- 114 Flexibilizer in insulating electric wires
- 115 Fluorescent lamps (interior coatings)
- 116 Glycerin-litharge cements for setting up electrical equipment, making conductive cements, etc.
- 117 Insulating tapes
- 118 Metal stripping (nickel from steel; gold from silver)
- 119 Microporous layers on electrodes
- 120 Oxide coated cathodes of luminescent tube
- 121 Preparing metals for use in batteries or accumulators
- 122 Retarding deterioration of oils in transformers, etc.
- ALKYDS
- 123 Battery cables
- 124 Binder for luminescent discharge tubes
- 125 Bonding agent in making insulators
- 126 Electromagnetic core laminations
- 127 Flexible insulators
- 128 Insulating cambric
- 129 Insulating paints
- 130 Molded caps for discharge tubes
- 131 Plating equipment coatings
- 132 Radio parts coatings and treatments
- 133 Resistance elements
- 134 Switchboard coatings
- 135 Wire coatings
- 136 X-ray equipment coatings

## Explosives

- 137 Dynamite
- 138 Nitroglycerin
- 139 Smokeless powders

## Glass, Ceramics, Abrasives

### A. Glass

- 140 Anti-mists and anti-fog compositions
- 141 Anti-mist pencils
- 142 Anti-shatter treatments during blasting or bombing
- 143 Cements (glycerin-litharge)
- 144 Chemical etchants (to control and localize action)
- 145 Decalcomania for ornamental effects
- 146 Fused labels and symbols
- 147 Glass inks
- 148 Glass polishes
- 149 Grinding and polishing glass, lenses, etc.
- 150 Laminant plasticizer for safety glass
- 151 Lens cleaners
- 152 Protective coatings
- 153 Sand-blast etching stencils (gelatin)
- 154 Scratch removers
- 155 Special putty, etc.
- 156 Special mirror compositions (colored mirrors)
- 157 Spray painting masks
- ALKYDS
- 158 Identifying marking paints
- 159 Laminants for safety glass
- 160 Metal-coated reflectors

- 161 Temporary protective coatings for polished surfaces
- 162 Vitreous decorative coatings

*B. Ceramics and Clay Products*

- 163 Abrasive massing clays
- 164 Acoustic plaster mixes
- 165 Binder for refractories
- 166 Bonding agents (glycerin-litharge)
- 167 Ceramic inks
- 168 Decalcomania designs
- 169 Glycerin-litharge lutes
- 170 Laboratory control or mill liquor
- 171 Modeling clay
- 172 Non-oily vitreous enamels
- 173 Porous building blocks
- 174 Silk screens for designs
- 175 Special materials for bonding metal to ceramics
- 176 Suspending media in decorative work
- 177 Temporary protective coatings
- 178 Underglaze effects

ALKYDS

- 179 Vitreous finishes for metals, etc.

*C. Abrasives*

- 180 Bonding agents for abrasives
- 181 Grinding and polishing stones (glycerin-litharge)
- 182 Massing material in manufacture of abrasive disks and wheels

- 183 Plasticizer for paper or cloth carriers
- 184 Razor sharpening compositions
- 185 Suspending medium for abrasives
- 186 Valve grinding compositions

ALKYDS

- 187 Bonding medium for abrasives

**Laboratory**

- 188 Acid-proofing corks
- 189 Bubble solutions for physical studies
- 190 Calibration of immersion refractometers
- 191 Chemical reagent
- 192 Clarifying agent
- 193 Comparison viscosimeters
- 194 Gas impervious seals
- 195 Gelatin models for photoelastic analysis of stresses
- 196 Glycerin-litharge cements for joining and repairing equipment
- 197 Heat transfer equipment
- 198 Lubricant in stopper boring
- 199 Maintaining sub-zero temperatures
- 200 Microscopic mountant
- 201 Mounting media for specimens
- 202 Organic-solvent-resistant lubricant for ground glass joints
- 203 Pressure transmitting equipment

- |     |  |     |   |
|-----|--|-----|---|
| 204 | Rubber tubing softener and preservative                        | 230 | Leather stuffing                        |
| 205 | Sealing media for organic solvents                             | 231 | Leather varnishes                       |
| 206 | Special heating baths  | 232 | Liming skins                            |
| 207 | Special flame tests  | 233 | Minimizes area changes due to weather   |
| 208 | Specimen preservation  | 234 | Patent leather softening preparations   |
| 209 | Suspending medium for grinding and matching glass joints, etc. | 235 | Polishes                                |
| 210 | Staining solutions for microscopy                              | 236 | Preventing drying out of chrome leather |
| 211 | Temporary seal for hydrogen                                    | 237 | Process material in leather printing    |
| 212 | "Unfreezing" glass stoppers and joints                         | 238 | Renovating processes                    |
|     |  | 239 | Saddle soaps                            |
|     |  | 240 | Seasoning compositions                  |
|     |  | 241 | Shoe cements                            |
|     |  | 242 | Shoe polishes and dressings             |

### Leather

- |     |  |     |   |
|-----|--|-----|---|
| 213 | Anti-static belt dressings             | 243 | Softener and flexibilizer prior to dressing |
| 214 | Artificial leathers and substitutes    | 244 | Specific glycerin treatments (e.g. samming) |
| 215 | Cements and glues                      | 245 | Supplies permanent moisture for pliability  |
| 216 | Coatings for leather rolls             | 246 | Tanning compositions                        |
| 217 | Dyeing and coloring compositions       | 247 | Waterproofing dressings                     |
| 218 | Fat liquors                            |     | ALKYDS                                      |
| 219 | Fur dyes and mordants                  | 248 | Laminating artificial leather               |
| 220 | Fur glosses                            | 249 | Leather finishes                            |
| 221 | Fur skin and leather tanning           |     |   |
| 222 | Harness dressings                      |     |   |
| 223 | Increases tensile strength and stretch |     |   |
| 224 | Inner sole compositions                |     |   |
| 225 | Leather belt dressings (anti-slip)     |     |   |
| 226 | Leather cleaners                       |     |   |
| 227 | Leather finishes and dressings         |     |   |
| 228 | Leather perfuming compositions         |     |   |
| 229 | Leather scrap utilization              |     |   |

### Lubricants

- |     |   |
|-----|---|
| 250 | Anti-static lubricants for belts, etc.            |
| 251 | Ball bearing lubricants                           |
| 252 | Bituminous dispersions                            |
| 253 | Clock mechanism lubricants                        |
| 254 | Desalting and demulsifiers for crude mineral oils |
| 255 | Emulsion lubricants                               |

- |     |   |     |   |
|-----|---|-----|---|
| 256 | Explosionproof lubricants   | 285 | ALKYDS  |
| 257 | Fire-resistant lubricants   | 286 | Lubricating compounds   |
| 258 | Food equipment lubricants   |     | Petroleum equipment coatings  |
| 259 | Gas meter lubricants  |     |   |
| 260 | Gasket pastes   |     |   |
| 261 | Gasoline pumping and processing equipment                                   |     |   |
| 262 | High-pressure lubricants  |     |   |
| 263 | Lime base greases   |     |   |
| 264 | Low-temperature lubricants  |     |   |
| 265 | Metal-drawing lubricants  |     |   |
| 266 | Molding-press lubricants  |     |   |
| 267 | Nitroglycerin explosives for starting and treating oil wells                |     |   |
| 268 | Oil well stimulating composition  |     |   |
| 269 | Organic-solvent-resistant lubricants  |     |   |
| 270 | Petroleum lubricants  |     |   |
| 271 | Pipe thread lubricants  |     |   |
| 272 | Plug valve lubricants   |     |   |
| 273 | Purifying crude or sludged oil  |     |   |
| 274 | Rubber lubricants   |     |   |
| 275 | Self-lubricating bearings   |     |   |
| 276 | Shock absorber lubricants   |     |   |
| 277 | Soda base greases   |     |   |
| 278 | Special lubricant with bentonite  |     |   |
| 279 | Special purpose oils and lubricants   |     |   |
| 280 | Strongly adherent greases   |     |   |
| 281 | Sweetening petroleum distillates  |     |   |
| 282 | Synthetic resin bearings  |     |   |
| 283 | Well drilling fluids and muds   |     |   |
| 284 | With graphite: in rubber lubricants, compressors, aircraft oxygen equipment |     |   |
|     |   |     | <b>Metals</b>   |
|     |   | 287 | Amalgam-electroplating (iron with precious metal)                       |
|     |   | 288 | Anodizing (coloring) aluminums  |
|     |   | 289 | Anti-corrosion compositions   |
|     |   | 290 | Casting molds   |
|     |   | 291 | Cleansing prior to painting, plating or enameling                       |
|     |   | 292 | Cold drawing lubricants   |
|     |   | 293 | Cutting oils and cutting oil emulsifiers                                |
|     |   | 294 | Derivatives; in ore flotation preparations                              |
|     |   | 295 | De-rusting compositions   |
|     |   | 296 | Electrolytic preparation of metals (iron, lead) from metallic salts     |
|     |   | 297 | Electroplating, polishing and stripping                                 |
|     |   | 298 | Galvanizing   |
|     |   | 299 | Glycerin-litharge for filling indentations                              |
|     |   | 300 | Glycerin-litharge mountants in metallurgical examination                |
|     |   | 301 | In etchants and compositions for micro-examination of metals and alloys |
|     |   | 302 | Ink for brass   |
|     |   | 303 | Marking crayons for hot metal surfaces                                  |
|     |   | 304 | Metals for use in batteries   |

- 305 Metal lacquers
- 306 Metal polishes
- 307 Nickel "plating" pastes
- 308 Protecting metals after pickling
- 309 Quenching medium for aluminum alloys
- 310 Sand mold binders
- 311 Stainless steel cleaners and polishes
- 312 Self-lubricating bearings
- 313 Steel-softening solutions
- 314 Soldering fluids and fluxes
- 315 Soldering pastes
- 316 Valve grinding compositions
- 317 Welding electrodes
- ALKYDS
- 318 Anti-corrosion paints
- 319 Anti-tarnish coatings for silver and brass
- 320 Baked foundry cores
- 321 Coatings to prevent weld spatter adhesion
- 322 Mold binders
- 323 Protective coatings

### Packaging Materials (Other Than Paper)

- 324 Bottle-sealing compositions (dip type)
- 325 Cellophane
- 326 Cellophane adhesives
- 327 Closure and label adhesives
- 328 Containers for oil (spiral chipboard, special laminated or otherwise treated paper)
- 329 Cork crown liners
- 330 Fiber containers (in laminants and adhesives)

- 331 Fiber cords and bands
- 332 Gasproof wrappings
- 333 Pellicles, bands and seals for bottles and jars
- 334 Plasticizer for composition liners
- 335 Rubber sealing rings
- 336 Sealing compositions
- 337 Transparent wrappings
- 338 Treating corks for wine bottles
- 339 Wrappings for frozen foods
- ALKYDS
- 340 Closures and metal ends of fiber containers
- 341 Waterproofing cellulosic films and sheets

### Paper

- 342 Acid-resistant papers
- 343 Anti-curl and anti-"dish" treatments
- 344 Bleaches
- 345 Bodying agent
- 346 Cloth-like papers
- 347 Cigarette papers (special)
- 348 Decalcomania papers
- 349 De-inking waste paper
- 350 Duplicating papers
- 351 Fireproofing papers
- 352 Flexibilizer
- 353 Glycerin-litharge cements for setting tile in digestors, sulfite liquor tanks, etc.
- 354 Greaseproof papers
- 355 High gloss finishes and varnishes
- 356 High-wet strength paper
- 357 Isolation of cellulosic sub-

- |  |     |  |
|--|-----|--|
| stances in ligneous raw materials                | 385 | Filter papers  |
| 358 Laminated paper and boards                   | 386 | Glaze finishes   |
| 359 Marbled paper                                | 387 | Greaseproofing finishes                                    |
| 360 Meat casings                                 | 388 | High wet strength papers                                   |
| 361 Moistureproof paper                          | 389 | Interiors of gasoline and water drums                      |
| 362 Oil impermeable paper and paper board        | 390 | Laminating compositions                                    |
| 363 Paper gaskets                                | 391 | Paper varnishes  |
| 364 Paper testers (Mullens burst tester)         | 392 | Polishing papers   |
| 365 Paper testing reagents and stains            | 393 | Sizing and impregnating compositions                       |
| 366 Parchment papers                             | 394 | Waterproof finishes  |
| 367 Pest-resistant papers                        | 395 | Water-resistant polishing papers                           |
| 368 Plasticizer and softener                     |     |  |
| 369 Plasticizer in waxed, glassine, etc., papers |     |  |
| 370 Plasticizing silicate coatings               |     |  |
| 371 Pulping processes                            |     |  |
| 372 Pulp testing equipment                       |     |  |
| 373 Rubber coatings                              |     |  |
| 374 Shrinkage retarding                          |     |  |
| 375 Sizing compositions                          |     |  |
| 376 Special food-wrapping papers                 |     |  |
| 377 Special finishes and coatings                |     |  |
| 378 Sterilizer                                   |     |  |
| 379 Temperature control of cooking liquors       |     |  |
| 380 Toweling, napkins, tissues (as softener)     |     |  |
| ALKYDS   |     |  |
| 381 Bank note papers                             |     |  |
| 382 Beater sizes (water-soluble alkyds)          |     |  |
| 383 Coatings for paper, paper board, etc.        |     |  |
| 384 Creped papers                                |     |  |
|  |     | <b>Photography</b>   |
|  | 396 | Anti-curling treatments for photos                         |
|  | 397 | "Anti-dazzle" coatings and coverings for photo-flash bulbs |
|  | 398 | Anti-dermatitis (e.g. metol) ointments                     |
|  | 399 | Anti-halation treatments                                   |
|  | 400 | Anti-dust measures for camera interiors                    |
|  | 401 | Bichromate processes                                       |
|  | 402 | Color photography emulsions                                |
|  | 403 | Creating special distortion effects                        |
|  | 404 | Diazo type films   |
|  | 405 | Eliminate air bells on film during developing              |
|  | 406 | Eliminate "Newton rings" in plate holders                  |
|  | 407 | Emulsion layer supporting materials                        |
|  | 408 | Film cabinet humidifier                                    |
|  | 409 | Fine focusing work transparentizing ground glass)          |

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| 410 | Formalin hardening baths<br>(motion picture film)                       | 436 | Stain removers   |
| 411 | Gelatin emulsions carrying<br>sensitizing materials                     | 437 | "Stay flat" formulas   |
| 412 | Gelatin stripping from<br>glass plates                                  | 438 | "Sticky-back" holders  |
| 413 | "Glycerin process" for<br>developing platinotype<br>prints              | 439 | "Touch up" compositions  |
| 414 | "High-light" effects  | 440 | Transparent adhesives  |
| 415 | Improver for deteriorated<br>negatives to create hard,<br>sharp effects | 441 | "Visible enlargement"<br>process   |
| 416 | Infra-red photography<br>coatings for flash bulbs                       |     | ALKYDS   |
| 417 | Kodachrome processing<br>and developing                                 | 442 | Carriers in "self develop-<br>able" films  |
| 418 | Local development on<br>bromide papers                                  | 443 | Color photography  |
| 419 | Masking pastes  | 444 | Emulsion carriers  |
| 420 | Motion picture threading<br>lubricant                                   | 445 | Film supports  |
| 421 | Mounting pastes   |     | <b>Plastics and Molding<br/>Compositions</b>   |
| 422 | Photographic papers   | 446 | Casein plastics plasticizer  |
| 423 | Photogravure  | 447 | Glue compositions for<br>molding purposes  |
| 424 | Photo plate-sinking   | 448 | Heating medium for<br>forming and shaping<br>acrylic plastics (for<br>bomber noses, gun blis-<br>ters, etc.) |
| 425 | Photoprinting on glass  | 449 | Imparting opalescence or<br>opacity to molded<br>phenolic products   |
| 426 | Pitting prevention in dry-<br>ing                                       | 450 | Lubricant for slicing<br>plastics  |
| 427 | Platinum print papers   | 451 | Massing material for horn<br>meal molding mixtures   |
| 428 | Preserver in pyro devel-<br>opers                                       | 452 | Melamine molding com-<br>positions   |
| 429 | Preventing ripples and<br>cracking                                      | 453 | Melamine resin-wood flour<br>combinations  |
| 430 | Print varnishes   | 454 | Mold lubricant   |
| 431 | Projection screens  | 455 | Plaster cast molds   |
| 432 | Rapid drying procedures   | 456 | "Plastic" wood or wood<br>doughs   |
| 433 | Repairing developer trays<br>(glycerin-litharge)                        | 457 | Plasticizer for regenerated<br>cellulose, etc.   |
| 434 | Restrainer inferrous oxal-<br>ate developer                             |     |  |
| 435 | Speeding up plate and<br>enlarger printing                              |     |  |



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| 458 Plasticizer for soybean protein plastics                                  | (fingers wet with glycerin)                           |
| 459 Sound record compositions   | 481 Fingerprint inks                                  |
| ALKYDS  | 482 Food-marking inks                                 |
| 460 Asbestos-filled molding compositions (with other resins)                  | 483 Fraud detector inks                               |
| 461 Binders in molding mixtures   | 484 General hygroscopic agent                         |
| 462 Brake linings   | 485 Hectograph inks                                   |
| 463 Clear and colorless cast products (with phenol-formaldehyde compositions) | 486 Hectograph pads and compositions                  |
| 464 Cores for metal molding   | 487 Indelible inks                                    |
| 465 Gaskets   | 488 Ink tablets                                       |
| 466 Linoleum  | 489 Instrument inks (for recording apparatus)         |
| 467 Mica bonding for insulation   | 490 Lithographic inks and varnishes                   |
| 468 Printing rollers  | 491 Lumber-marking inks                               |
| <b>Printing, Lithography, Inks, etc.</b>                                      | 492 Maintaining requisite humidity in printing plants |
| 469 Adhesion promoter for printing on glossy paper                            | 493 Marking inks                                      |
| 470 Anti-oxidant  | 494 Manifold sheets                                   |
| 471 Carbon and other duplicating papers                                       | 495 Mercurographic tusches                            |
| 472 Collotype printing processes  | 496 Multigraph inks                                   |
| 473 Conditioning printing rollers   | 497 Offset preventer                                  |
| 474 Conductive inks   | 498 Opacity promoter                                  |
| 475 Decalcomania compositions   | 499 Pencil leads                                      |
| 476 Design transfer solutions   | 500 Photo-engraved intaglio plates                    |
| 477 Drawing inks  | 501 Plate-etching compositions                        |
| 478 Duplicator inks   | 502 Printers' blankets                                |
| 479 Embossing inks  | 503 Printing inks                                     |
| 480 Facilitating paper handling during printing                               | 504 Printers' rollers (glycerin type)                 |
|   | 505 Protecting litho plates during storage            |
|   | 506 Reducing agent                                    |
|   | 507 Restoring charred documents                       |
|   | 508 Restoring old and dried inks                      |
|   | 509 Restrainer in quick-drying inks                   |
|   | 510 Secret-writing detection                          |

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| 511 Sensitized printing plates                                     | 537 Body finishing rosin   |
| 512 Silk screen printing   | 538 De-icing coatings for air-<br>plane surfaces                               |
| 513 Show card inks   | 539 Esterification of lignin<br>liquors for use in pro-<br>tective coatings    |
| 514 Spreading agent  | 540 Glycerin rosin   |
| 515 Stamp pad inks   | 541 Metal lacquers (simple<br>gum solutions)                                   |
| 516 Static elimination during<br>printing                          | 542 Oil-lac (shellac) varnishes  |
| 517 Stencil inks   | 543 Paint hardener   |
| 518 Sterilizer to prevent mold<br>formation                        | 544 Removing moisture from<br>paint spray compressed<br>air lines              |
| 519 "Sympathetic" inks (in-<br>visible inks)                       | 545 Rubbing varnish rosin  |
| 520 Thickener  | 546 Shellac dispersions<br>(aqueous)   |
| 521 Toner  | 547 Softener in artists' colors  |
| 522 Transfer papers in litho-<br>graphy                            | 548 Starting material in manu-<br>facture of alkyd resins<br>and ester gums    |
| 523 Transference foils   | 549 Synthetic "drying" oils to<br>replace tung oil, etc.                       |
| 524 Typewriter ribbons and<br>inks                                 | 550 White carbonate rosin  |
| 525 Writing inks   |  |
| ALKYDS   |  |
| 526 Drawing utensils   |  |
| 527 Fortifying agents in litho<br>varnishes and inks               |  |
| 528 Gloss inks   |  |
| 529 Gloss overprint varnishes                                      |  |
| 530 Half-tone blacks and<br>process inks                           |  |
| 531 Non-scratch inks   |  |
| 532 Printing and lithographic<br>inks for metals, etc.             |  |
| 533 Printing inks  |  |
| 534 Printers' rollers  |  |
| 535 White-writing boards (for<br>classrooms, etc.)                 |  |
| Protective Coatings<br>(Paints, Varnishes<br>Lacquers and Enamels) |  |
| 536 "Aquarell" colors<br>(water-soluble)                           |  |
|  | 551 Aircraft decalcomania  |
|  | 552 Airplane coatings  |
|  | 553 Architectural finishes   |
|  | 554 Automobile paints and<br>finishes  |
|  | 555 Baked finishes—enamels   |
|  | 556 Baked finishes for spray<br>applications                                   |
|  | 557 Baking primers   |
|  | 558 Bond coats in metal deco-<br>rating  |
|  | 559 Bridge paints  |
|  | 560 Camouflage paints  |
|  | 561 Coatings on leather, cloth,<br>paper, rubber, composi-<br>tion board, etc. |

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| 562 | Dye-resistant coatings for textile coloring supports | 590 | Rust-inhibiting primers  |
| 563 | Enamels (gloss, semi-gloss, lusterless)              | 591 | Shingle stains   |
| 564 | Engine finishes                                      | 592 | Sign finishes  |
| 565 | Flexible rubber lacquers                             | 593 | Simulated hammered metal finishes  |
| 566 | Fortifying interior house paints                     | 594 | Spar varnishes   |
| 567 | Furniture lacquers and varnishes                     | 595 | Steel furniture enamels  |
| 568 | Fungus-resistant paints                              | 596 | Tank and gun finishes  |
| 569 | Hardware finishes                                    | 597 | Truck enamels  |
| 570 | Heat-resistant insulating varnishes                  | 598 | Two-tone finish  |
| 571 | Industrial finishes                                  | 599 | Urea formaldehyde-alkyd combinations   |
| 572 | Machine finishes                                     | 600 | Varnishes  |
| 573 | Maintenance paints                                   | 601 | Vehicles for aluminum powders  |
| 574 | Marine finishes (interior and exterior)              | 602 | Wood sealers   |
| 575 | Modifiers for other synthetic resins (e.g., ureas)   | 603 | Wrinkle finishes   |
| 576 | Nitrocellulose and lacquer sealers                   |     | ALKYD RESIN EMULSIONS  |
| 577 | Nitrocellulose lacquer plasticizers                  | 604 | Exterior paints (for cinderblock, brick, concrete, stucco, masonry, etc.)        |
| 578 | Numeral and process colors                           | 605 | Interior wall paints (homes, apartments, etc.)                                   |
| 579 | Outdoor wood finishes                                | 606 | Shellac substitutes  |
| 580 | Paints for preventing ice formation                  |     | ESTER GUMS   |
| 581 | Paints for toys                                      | 607 | Greaseproof baking enamels   |
| 582 | Primer grounds for repainting                        | 608 | Nitrocellulose lacquers  |
| 583 | Primers, undercoats and finishes for metals          | 609 | Varnishes (e.g., "spar" varnishes)   |
| 584 | Pump enamels   |     | Rubber   |
| 585 | Railroad and freight car finishes                    | 610 | Air bag treatments and coatings to prevent adhesion, sulfur migration and ageing |
| 586 | Refrigerator, etc., enamels                          | 611 | Anti-drying agent  |
| 587 | Road-marker enamels                                  |     |  |
| 588 | Roller coatings                                      |     |  |
| 589 | Roof and barn paints                                 |     |  |

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| 612 | Anti-skid compositions and treatments                                   | 636 | Rubber dispersions for coating and impregnating                            |
| 613 | Bicycle tire fillers  | 637 | Rubber-marking ink   |
| 614 | Centers for golf balls  | 638 | Rubber preservatives   |
| 615 | Composition for reinforcing tire tubes                                  | 639 | Rubber thread formation  |
| 616 | Compositions for separating tacky rubber sheets or parts                | 640 | Softener and flexibilizer  |
| 617 | Conditioning agent  | 641 | Tire-sealing compositions  |
| 618 | Derivatives employed as anti-oxidants                                   | 642 | Treating tire cords  |
| 619 | Devulcanizers   | 643 | Vulcanizing accelerator assistant  |
| 620 | Electrodeposition of rubber from latex                                  |     | ALKYDS   |
| 621 | Formulation of "artificial" rubbers                                     | 644 | Anti-scorch agents   |
| 622 | "Gum" erasers   | 645 | Artificial rubber  |
| 623 | Increasing oil resistance of rubber                                     | 646 | Gas tight coatings   |
| 624 | Latex preservatives   | 647 | In rubber dollies of dry cells   |
| 625 | Latex sealing composition for containers                                | 648 | Oil resistant coatings for rubber surfaces (e.g., hoses, oil line gaskets) |
| 626 | Lubricants  | 649 | Protective coatings  |
| 627 | Medium for ultra-rapid vulcanization at high temperatures and pressures | 650 | Rubber and latex extenders (for both natural and synthetic)                |
| 628 | Mixes for vulcanizing rubber  | 651 | Tire retreading  |
| 629 | Mold lubricants and anti-stick compositions                             | 652 | Water and gas impermeable coatings   |
| 630 | Polyvinyl alcohol plasticizer (substitute)                              |     | <b>Textiles</b>  |
| 631 | Protective coatings and paints  | 653 | Anti-mold and anti-rot compositions  |
| 632 | Reducing electrostatic properties                                       | 654 | Anti-shrinkage treatments for wool   |
| 633 | Renovating rubber goods   | 655 | Asbestos cloth substitutes   |
| 634 | Rubber and latex threads (as flexibilizer)                              | 656 | Bast fiber treatments  |
| 635 | Rubber-containing adhesives   | 657 | Bleaching natural straws   |
|     |   | 658 | Bleaching processes  |
|     |   | 659 | Color lakes (e.g., titanium)   |
|     |   | 660 | Crease-resistant finishes  |
|     |   | 661 | Degumming silk   |

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| 662 | Dyeing compositions (dye solvent)                                | various dyestuffs, leveling and stripping assistants, etc.    |
| 663 | Dyeing natural straws and fibers                                 |   |
| 664 | Ester gums for increased body, fullness and stiffness            | 686 Rayon de-lustering  |
| 665 | Fabric-marking and identifying inks                              | 687 Rubberized fabrics  |
| 666 | Fabric-weighting compositions                                    | 688 Screen printing   |
| 667 | Felt manufacture   | 689 Sizing compositions                                       |
| 668 | Fireproofing treatments  | 690 Softening treatments for artificial fibers                |
| 669 | Gasproofing treatment  | 691 Softening treatments for straw and fibers                 |
| 670 | Giving viscose a wooly character                                 | 692 Softening treatments for silk                             |
| 671 | Glycerinated feathers for millinery                              | 693 Solventproofing treatments                                |
| 672 | Imparting soft handle to wool, etc.                              | 694 Soybean protein fibers (as flexibilizer)                  |
| 673 | Increasing snag and pull resistance                              | 695 Spray dyeing silk and rayon                               |
| 674 | Increasing wearability   | 696 Steaming and aging treatments                             |
| 675 | In manufacture of fibers from milk                               | 697 Tailor's chalk  |
| 676 | In manufacture of rayon and other cellulosic fibers              | 698 Textile adhesives (for uniting cloth plies)               |
| 677 | Laboratory aid in study and identification of fibers and fabrics | 699 Textile detergent, wetting and emulsifying agents         |
| 678 | Mercerizing lyes   | 700 Textile finishes  |
| 679 | Pigment dispersions  | 701 Textile oils and lubricants                               |
| 680 | Plasticizer for pyroxylin finishes                               | 702 Thickening agents for printing pastes                     |
| 681 | Preservative and anti-septic                                     | 703 Vat dyeing  |
| 682 | Printing imitation fur effects                                   | 704 Waterproofing treatments                                  |
| 683 | Printing pastes  | 705 Wool substitutes  |
| 684 | Printing resists   |   |
| 685 | Process material and starting point in making                    | ALKYDS  |
|     |  | 706 Binders for pigments                                      |
|     |  | 707 Bonding cloth plies (for making semi-stiff collars, etc.) |
|     |  | 708 Chintz effects  |
|     |  | 709 Coated cloth for pump diaphragms, etc.                    |
|     |  | 710 Coating dye supports                                      |

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| 711 | Dyeing compositions   | 736 | Paints for marking<br>wooden containers         |
| 712 | Gasproofed fabrics  | 737 | Paints, varnishes,<br>lacquers, etc.            |
| 713 | Insulating cambric  | 738 | Plasticizing veneers for<br>decorative purposes |
| 714 | Linoleum-like floor and<br>wall coverings   | 739 | "Plastic wood" for repair<br>work               |
| 715 | Non-slip finishes on rayon  | 740 | Preservative compositions                       |
| 716 | "Oiled silk" substitute for<br>bandages   | 741 | Preserving decorative<br>foliage (indoor uses)  |
| 717 | Plasticizer for other<br>plastic coating materials  | 742 | Renovating treatments                           |
| 718 | Printing pastes   | 743 | Rot-preventing prepara-<br>tions                |
| 719 | Rubber coatings and im-<br>pregnations  | 744 | Veneer-patching adhesive                        |
| 720 | Sizings   | 745 | Veneer sizes                                    |
| 721 | Special finishes  | 746 | Waterproofing composi-<br>tions                 |
| 722 | Special treatments for<br>sheer fibers (as in rayon<br>or silk stockings) to pre-<br>vent snags and pulled<br>threads | 747 | Wood-laminating adhe-<br>sives (Plywood)        |
| 723 | Textile varnishes   |     |   |
| 724 | Transparent and imperme-<br>able coatings   |     |   |
| 725 | Wash-resistant glaze<br>finishes  |     |   |
| 726 | Waterproofing fabrics   |     |   |
| 727 | Weather-resistant netting   |     |   |

### Wood

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| 728 | Anti-termite treatments                                   | 750 | Anti-freeze in gas meters  |
| 729 | Bleaching wood  | 751 | Automatic gas monitors   |
| 730 | Coating to prevent adhe-<br>sion of ice                   | 752 | Automatic helmsman for<br>yachts and small ships   |
| 731 | Cork substitutes  | 753 | Bituminous road dressings  |
| 732 | Glues and other adhesives                                 | 754 | Boiler scale retarders and<br>removers   |
| 733 | Imparting special grain<br>effects                        | 755 | Bright flame lamp oil  |
| 734 | Improving pliability of<br>wood in barrel making,<br>etc. | 756 | Catgut and tennis string<br>preservative   |
| 735 | Molding compositions for<br>decorative work               | 757 | Cellophane capes for mak-<br>ing protective clothing<br>for workers (also gas-<br>proof capes for<br>soldiers) |

### Miscellaneous

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|-----|---|-----|--|
| 758 | Dehydration of natural gases                                  | 782 | Producing anhydrous alcohol  |
| 759 | Doll manufacture  | 783 | Pump packings  |
| 760 | Door-closure control fluids                                   | 784 | Recoil absorption in stamping machines                               |
| 761 | Emulsifying agents  | 785 | Roofing mastic (bituminous bases, to prolong setting time)           |
| 762 | Filler for wells of mercury-in-glass thermometers             | 786 | Sealing orifice meters to prevent freezing                           |
| 763 | Gas mask cannister compositions                               | 787 | Ships' steering gear   |
| 764 | Glossy plaster-cement mixes                                   | 788 | Softening sponges  |
| 765 | Gun recoil mechanisms   | 789 | Stable foams for preventing evaporation of gasoline in storage tanks |
| 766 | Hydraulic machinery   | 790 | Starting point in manufacture of numerous chemical derivatives       |
| 767 | Ice-simulating compositions                                   | 791 | Suction-cup aid  |
| 768 | Jute packings   | 792 | Wall sizings   |
| 769 | Linoleum manufacture  | 793 | Wax substitutes  |
| 770 | Luminous crayons  |     | <b>Agriculture</b>   |
| 771 | Manometer seal pots in oil cracking equipment (winter)        | 794 | Animal protection against poison gas                                 |
| 772 | Manufacture of matches  | 795 | Ant poisons  |
| 773 | Maritime and aeronautical compasses                           | 796 | Anti-"fly-strike" compositions                                       |
| 774 | Non-freezing fire extinguishers                               | 797 | Antifreeze plant sprays  |
| 775 | Non-slip compositions for rugs and carpets                    | 798 | Canker treatment for plants and trees                                |
| 776 | Outdoor sprinkler systems (to prevent freezing during winter) | 799 | Cauterizing cut seed potato  |
| 777 | Phonographic disk-cutting machinery                           | 800 | Cod-liver-oil emulsions for cattle                                   |
| 778 | Plaster compositions (for construction)                       | 801 | Colchicine plant treatments  |
| 779 | Poison gas-detecting solutions (bromine and chlorine)         | 802 | Conditioning agent for plant leaves                                  |
| 780 | Preserving book bindings (leather)                            | 803 | Egg-marking inks   |
| 781 | Pressure regulators on boilers (compensator)                  | 804 | Fertilizers  |
|     |   | 805 | Fire blight treatments for trees                                     |

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| 806 | Flypaper (sticky and poison types)           |     | ener, clarifying and maturing agent                   |
| 807 | Freshener for indoor plants                  | 834 | Coloring compositions                                 |
| 808 | Glossing feathers and furs for prize animals | 835 | Diabetic lemonade, etc.                               |
| 809 | Insecticidal sprays and mists                | 836 | Flavoring emulsions, bases, etc.                      |
| 810 | Insecticidal white washes                    | 837 | Flavoring extracts                                    |
| 811 | Insect poison fluids (for cracks, etc.)      | 838 | Flavoring syrups                                      |
| 812 | Nicotine fumigants for greenhouses           | 839 | Foam extracts   |
| 813 | Packing material for plant shipping          | 840 | Fountain syrups                                       |
| 814 | Parasiticial sprays                          | 841 | Holland gin   |
| 815 | Pest baits and poisons                       | 842 | Liqueur formulation                                   |
| 816 | Plant growth stimulants                      | 843 | "Mineralizing" beverages with glycerophosphates       |
| 817 | Potato rot control                           | 844 | Mixed drink smoothing agent                           |
| 818 | Poultry perch insecticide                    | 845 | Natural component of wines                            |
| 819 | Protective compounds for nursery stock       | 846 | Non-alcoholic flavoring extracts                      |
| 820 | Red spider spray (alkyd)                     | 847 | "Pick-me-up" bitters                                  |
| 821 | Rodent repellents                            | 848 | Scotch whiskey base flavor                            |
| 822 | Seed disinfectants                           | 849 | Soft drink manufacture                                |
| 823 | Seedling shipping                            | 850 | Soluble coffee extracts                               |
| 824 | Seed treatments (e.g., stimulation)          | 851 | Sterilizing agent for wines                           |
| 825 | Sheep and other dips                         | 852 | Triacetin (derivative) as flavor solvent and fixative |
| 826 | Soilless growing processes                   | 853 | Vanilla extracts                                      |
| 827 | Spray control                                | 854 | Whiskey blending and "smoothing"                      |
| 828 | Tree protective against rabbits, etc.        | 855 | Wine analysis   |
| 829 | Tree wound treatments                        | 856 | Wine clarification and improvement                    |
| 830 | Veterinary remedies                          |     |   |

### Beverages

- 831 After-fermentation suppressor for wines
- 832 Artificial flavor bases and essences
- 833 Brewing products sweet-

### Chiropody and Podiatry

- 857 Adhesive tapes and plasters
- 858 Antiperspirants
- 859 Antipruritics
- 860 Antiseptics
- 861 Bunion paints



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| 862 | Chiropodists' pastes                            | 892 | Mouth washes and gargles                      |
| 863 | Collodion preparations<br>(e.g., Kelly's paint) | 893 | Nit-destroying lotion                         |
| 864 | Corn and callus pads and<br>rings               | 894 | Shampoos                                      |
| 865 | Corn and callus ointments<br>and gels           | 895 | Shaving preparations                          |
| 866 | Corn caustics                                   | 896 | Skin protectives                              |
| 867 | Cuticle softeners                               | 897 | Soaps   |
| 868 | Deodorants                                      | 898 | Stain, lacquer, etc.,<br>removers (from skin) |
| 869 | Foot creams and oint-<br>ments                  | 899 | Synthetic detergents                          |
| 870 | Frost bite remedies                             | 900 | Toilet deodorants                             |
| 871 | Fungicidal ("athlete's<br>foot") products       | 901 | Transparent glycerin<br>soaps                 |
| 872 | Glycerin gelatin films and<br>coatings          | 902 | "Waterless" cleansers                         |
| 873 | Glycerite of tannic acid                        | 903 | Water softener                                |
| 874 | Lotion of camphor and<br>chloral                |     |   |
| 875 | Massaging preparations                          |     |   |
| 876 | Nail bleaches                                   |     |   |
| 877 | Nail softening compounds                        |     |   |
| 878 | Ointment bases                                  |     |   |
| 879 | Protective ointments                            |     |   |
| 880 | Soothing lotions                                |     |   |

### **Cosmetics and Toilet Preparations**

### **Cleanliness, Sanitation and Personal Hygiene**

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|-----|---|-----|------------------------------------|
| 881 | Abrasive soaps (industrial<br>hand cleansers) | 904 | Acid creams                        |
| 882 | Bath fluids                                   | 905 | Acne creams                        |
| 883 | Bath salts                                    | 906 | After-shave lotions                |
| 884 | Cleaning pads (cosmetic)                      | 907 | "All-purpose" creams               |
| 885 | Dentifrices (pastes and<br>liquids)           | 908 | Almond creams                      |
| 886 | Disinfectants                                 | 909 | Alum pencils                       |
| 887 | Douches                                       | 910 | Astringent creams                  |
| 888 | Foam or bubble baths                          | 911 | Astringent lotions                 |
| 889 | Hand cleaners                                 | 912 | Bath fluids                        |
| 890 | Insecticides                                  | 913 | Bath salts                         |
| 891 | Liquid soaps                                  | 914 | Bay rum                            |
|     |   | 915 | Beard softeners                    |
|     |   | 916 | Beauty milks                       |
|     |   | 917 | Bleaching creams                   |
|     |   | 918 | Blemish-covering compo-<br>sitions |
|     |   | 919 | Brilliantines                      |
|     |   | 920 | Bubble baths                       |
|     |   | 921 | "Bust developers"                  |
|     |   | 922 | Cake powders                       |
|     |   | 923 | Chap-relieving compounds           |
|     |   | 924 | Cleansing creams                   |
|     |   | 925 | Cleansing lotions                  |
|     |   | 926 | Cleansing pads                     |
|     |   | 927 | Cold creams                        |

## 230 *Glycerin—Its Industrial and Commercial Applications*

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|-----|--|-----|---|
| 928 | Concentrated cosmetic<br>creams            | 965 | Lubricating creams                                |
| 929 | Corrective cosmetics (e.g.,<br>blackheads) | 966 | Machineless permanent<br>waves                    |
| 930 | Cosmetic emulsifiers                       | 967 | Manicure preparations                             |
| 931 | Cosmetic stockings                         | 968 | Mascaras  |
| 932 | Cream colognes                             | 969 | Massage creams                                    |
| 933 | Cream rouges                               | 970 | Matt creams                                       |
| 934 | Cuticle remover                            | 971 | Mustache wax                                      |
| 935 | Cuticle softener                           | 972 | Nail bleaches                                     |
| 936 | Depilatories                               | 973 | Nail creams                                       |
| 937 | Deodorant liquids, pastes<br>and creams    | 974 | Nail enamel                                       |
| 938 | Electric shaver lotions                    | 975 | Nail polish remover pads                          |
| 939 | Eyebrow liquid colors                      | 976 | Nail polish removers                              |
| 940 | Facial masks                               | 977 | Nail white  |
| 941 | Foundation creams                          | 978 | Non-alcoholic lotions                             |
| 942 | Freckle creams                             | 979 | Permanent wave lotions                            |
| 943 | Glycerin creams and gels                   | 980 | Pomades   |
| 944 | Greaseless lip rouge sticks                | 981 | Powder bases                                      |
| 945 | Hair dyeing compositions                   | 982 | Powder creams                                     |
| 946 | Hair dye remover                           | 983 | Scalp ointments and<br>lotions                    |
| 947 | Hair lacquers; hair<br>pomades             | 984 | Shampoos  |
| 948 | Hair "restorers"                           | 985 | Shaving creams (lathering<br>and brushless types) |
| 949 | Hair-setting jellies                       | 986 | Shaving sticks                                    |
| 950 | Hair tonics                                | 987 | Skin protectives                                  |
| 951 | Hair-waving fluids                         | 988 | Skin reconditioners                               |
| 952 | Hand creams                                | 989 | Skin toners and "tonics"                          |
| 953 | Hand lotions                               | 990 | Soapless shampoos                                 |
| 954 | Hormone creams                             | 991 | "Solidified" glycerin                             |
| 955 | Hypo-allergic cosmetics                    | 992 | Suntan preparations                               |
| 956 | Insect repellants (creams<br>and lotions)  | 993 | Suntan simulating prepa-<br>rations               |
| 957 | Kinky hair dressings                       | 994 | Toothpastes and liquid<br>dentifrices             |
| 958 | Lanette wax-containing<br>cosmetics        | 995 | Vanishing creams                                  |
| 959 | Lecithin creams                            | 996 | Vitamin-containing cos-<br>metics                 |
| 960 | Lemon juice cosmetics                      | 997 | Wrinkle creams                                    |
| 961 | Lip jellies                                |     |   |
| 962 | Liquid creams                              |     |   |
| 963 | Liquid powders                             |     |   |
| 964 | Liquid rouges                              |     |   |

### Dentistry

- |     |                      |
|-----|----------------------|
| 998 | Abrasive polishes    |
| 999 | Antiseptic solutions |

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|---|---|
| 1000 Artificial denture materials (alkyds and other materials)  | 1029 Mold lubricants                                    |
| 1001 Astringents  | 1030 "Moldine" and other plastic clays                  |
| 1002 Bleaching teeth  | 1031 Molding-press lubricants                           |
| 1003 Copper tempering   | 1032 Molding sands                                      |
| 1004 Correctives  | 1033 Mouth washes                                       |
| 1005 Counter-irritants  | 1034 Novocaine dermatitis lotions                       |
| 1006 Crown and plate swager compounds                           | 1035 Operative antiseptics                              |
| 1007 Dental pharyngitis preparations                            | 1036 Oral medication solvent and vehicle                |
| 1008 Dentifrices, liquid  | 1037 Pain relievers (e.g., from "dry socket")           |
| 1009 Dental pulp devitalizing compounds                         | 1938 Post-operative care products                       |
| 1010 Dental pulp digestants                                     | 1039 Pre-injection mucous membrane cleaners             |
| 1011 Denture irritation soothing agent                          | 1040 Prophylaxis pastes                                 |
| 1012 Denture polishes   | 1041 Prosthetic compositions                            |
| 1013 Desensitizing dentin (fluoride treatment)                  | 1042 Protectives for skin and mucous membranes          |
| 1014 Disclosing solutions                                       | 1043 Pulp mummifying pastes                             |
| 1015 "Dry socket" treatments                                    | 1044 Pyorrhea treatments                                |
| 1016 Duplicating molds  | 1045 Resin prosthetic materials (alkyd resins)          |
| 1017 Enamel-protective solutions (during orthodontic treatment) | 1046 Rinsing solutions                                  |
| 1018 Facial casts   | 1047 Root-canal-filling materials                       |
| 1019 Facial-defect-restoring compositions                       | 1048 Root-canal sealers                                 |
| 1020 Fetid breath products                                      | 1049 Rubber items conservation                          |
| 1021 Foil substitute in dental plate curing                     | 1050 Stomatitis-treating compositions                   |
| 1022 Gingivitis-treating preparations                           | 1051 Styptics   |
| 1023 Gum paints in tooth infections                             | 1052 Styptic cotton                                     |
| 1024 Hand creams for dentists                                   | 1053 Sulfonamide treatments                             |
| 1025 Impression materials                                       | 1054 Teeth removal from vulcanite dentures              |
| 1026 Instrument sterilizing solution                            | 1055 Toothache drops                                    |
| 1027 Instrument lubricant                                       | 1056 Toothpastes  |
| 1028 Massage fluids for gums                                    | 1057 Tooth soaps  |
|   | 1058 Tongue-treating compositions (e.g., for glossitis) |

- 1059 Vincent's angina treatment  
1060 Vulcanizing medium in making prosthetics

### Diagnosis, Laboratory and Clinical

- 1061 Allergy-diagnostic extracts  
1062 Bacteriological-culture media  
1063 Bacterial-specimen shipment  
1064 Blood-count-diluting fluid  
1065 Blood film stains  
1066 Blood urea determination  
1067 Diagnostic test for small-pox  
1068 Differential staining  
1069 Dust deposit surveys (re: air contamination)  
1070 Electrocardiography jellies  
1071 Glucose determinations  
1072 Histological preparations  
1073 Imbedding materials  
1074 Instrument recording inks (basal metabolism, etc.)  
1075 Laboratory reagent  
1076 "Match" test  
1077 Mounting medium for microscopy  
1078 Patch tests  
1079 Pollen counting and surveying  
1080 Serum preservation (for Wasserman test)  
1081 Skin scratch tests in allergy  
1082 Specimen clarification

- 1083 Specimen preservation  
1084 Sputum concentration  
1085 Staining solutions for microscopy  
1086 Tellurite test for diphtheria  
1087 Tuberculins

### Drugs and Pharmaceuticals \*

- U. S. PHARMACO-  
POEIA XII  
PREPARATIONS  
1088 Elixir of phenobarbital  
1089 Extract of malt  
1090 Fluid extracts, process B  
1091 Glycerinated gelatin  
1092 Glycerite of tannic acid  
1093 Glycerite of starch  
1094 Glycerite of boroglycerin  
1095 Glyceryl triacetate (triacetin)  
1096 Liquor chloroazodin  
1097 Mucilage of tragacanth  
1098 Pills of ferrous carbonate  
1099 Medicinal soft soap  
1100 Liniment of soft soap (tincture of green soap)  
1101 Spirit of glyceryl trinitrate  
1102 Glycerin suppositories  
1103 Syrup of ipecac  
1104 Syrup of wild cherry  
1105 Glyceryl trinitrate tablets  
1106 Compound tincture of cardamon  
1107 Compound tincture of gentian  
1108 Aromatic tincture of rhubarb  
1109 Old tuberculin (tuberculin-Koch)

\* Medical and health-conserving uses given in the order of their appearance in the U.S.P. XII and N.F. VII.

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|------|---|------|---|
| 1110 | Tannic acid ointment                              | 1137 | serenoa and sandalwood                    |
| 1111 | Iodine ointment                                   | 1138 | Compound elixir of taraxacum              |
| 1112 | Smallpox vaccine                                  | 1139 | Elixir of terpin hydrate                  |
|      | NATIONAL  | 1140 | Elixir of terpin hydrate and codeine      |
|      | FORMULARY VII                                     | 1141 | Compound elixir of vanillin               |
|      | PREPARATIONS                                      | 1142 | Compound elixir of viburnum opulus        |
| 1113 | Calcium glycerophosphate                          | 1143 | Elixir of viburnum prunifolium            |
| 1114 | Elixir aminopyrine                                | 1144 | Ferric glycerophosphate                   |
| 1115 | Elixir of barbitol                                | 1145 | Fluidextracts, process B                  |
| 1116 | Elixir of bismuth                                 | 1146 | Fluidextract of castanea                  |
| 1117 | Elixir of calcium and sodium                      | 1147 | Fluidextract of hammelis leaf             |
| 1118 | Glycerophosphates                                 | 1148 | Fluidextract of krameria                  |
| 1119 | Compound elixir of euphorbia                      | 1149 | Fluidextract of wild cherry               |
| 1120 | Elixir of iron, quinine and strychnine            | 1150 | Fluidextract of rose                      |
| 1121 | Elixir of iron, quinine and strychnine phosphates | 1151 | Compound fluidextract of sarsaparilla     |
| 1122 | Elixir of gentian                                 | 1152 | Fluidextract of taraxacum                 |
| 1123 | Elixir of gentian and iron                        | 1153 | Fluid glycerates                          |
| 1124 | Glycerinated elixir of gentian                    | 1154 | Gargle of potassium chlorate with iron    |
| 1125 | Compound elixir of glycerophosphates              | 1155 | Jelly of ephedrine sulfate                |
| 1126 | Elixir of guarana and celery                      | 1156 | Glycerite of bismuth                      |
| 1127 | Elixir of hydrangea and lithium                   | 1157 | Glycerite of iodine and zinc iodide       |
| 1128 | Low-alcohol elixir                                | 1158 | Glycerite of egg yolk                     |
| 1129 | High-alcohol elixir                               | 1159 | Glycerite of phenol                       |
| 1130 | Elixir of pepsin                                  | 1160 | Glycerite of tragacanth                   |
| 1131 | Elixir of pepsin, bismuth and strychnine          | 1161 | Glycerogelatin                            |
| 1132 | Compound elixir of pepsin                         | 1162 | Solution of carmine                       |
| 1133 | Elixir of pepsin and bismuth                      | 1163 | Solution of cochineal                     |
| 1134 | Elixir of pepsin and rennin                       | 1164 | Solution of iron and ammonium acetate     |
| 1135 | Elixir of phosphorus                              | 1165 | Solution of peptonized iron               |
| 1136 | Compound elixir of                                | 1166 | Solution of peptonized iron and manganese |
|      |   | 1167 |   |

234 *Glycerin—Its Industrial and Commercial Applications*

- |      |   |      |   |
|------|---|------|---|
| 1168 | Phenolated solution of iodine             | 1196 | Tincture of rhubarb                         |
| 1169 | Solution of nux vomica alkaloids          | 1197 | Sweet tincture of rhubarb                   |
| 1170 | Compound solution of sodium borate        | 1198 | Compound tincture of viburnum               |
| 1171 | Solution of sodium phosphate              | 1199 | Compound ointment of resorcinol             |
| 1172 | Calamine lotion                           | 1200 | Clinical diagnosis preparations             |
| 1173 | Phenolated lotion of calamine             | 1201 | Toisson's fluid (blood diluent)             |
| 1174 | Manganese glycerophosphate                | 1202 | Haines' solution (for dextrose)             |
| 1175 | Mass of mercury                           | 1203 | Glycerin bouillon (culture medium)          |
| 1176 | Honey of rose and sodium borate           | 1204 | Glycerin agar (culture medium)              |
| 1177 | Compound mixture of opium and glycyrrhiza | 1205 | Bordet-Gengou potato medium                 |
| 1179 | Mixture of rhubarb and soda               | 1206 | Corper's medium                             |
| 1180 | Pectin paste                              | 1207 | Petroff's medium                            |
| 1181 | Thin pectin paste                         | 1208 | Delafield's hematoxylin (staining) solution |
| 1182 | Pills of aloe and mastic                  | 1209 | Pappenheim's solution                       |
| 1183 | Sodium glycerophosphate                   | 1210 | Giemsa's staining solution                  |
| 1184 | Suppositories of boro-glycerin            | 1211 | Glycerin (mounting) jelly                   |
| 1185 | Syrup of althea                           | 1212 | Adhesive tapes and plasters                 |
| 1186 | Syrup of ammonium hypophosphite           | 1213 | Alginate gels                               |
| 1187 | Syrup of calcium lactophosphate           | 1214 | Allergenic preparations for desensitization |
| 1188 | Syrup of hypophosphites                   | 1215 | Alteratives                                 |
| 1189 | Compound syrup of hypophosphites          | 1216 | Amebicides (in amebiasis)                   |
| 1190 | Compound syrup of white pine              | 1217 | Analgesic ointments                         |
| 1191 | Compound tincture of cinchona             | 1218 | Anesthetics, local                          |
| 1192 | Tincture of cinnamon                      | 1219 | Anesthetics, parenteral                     |
| 1193 | Acetic tincture of larkspur               | 1220 | Antacid solutions                           |
| 1194 | Compound tincture of gambir               | 1221 | Antacids                                    |
| 1195 | Tincture of kino                          | 1222 | Anthelmintics                               |
|      |   | 1223 | Antiperspirants                             |
|      |   | 1224 | Antiphlogistines                            |
|      |   | 1225 | Antiseptic preparations                     |
|      |   | 1226 | Antiseptic washes                           |

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|------|---|------|---|
| 1227 | Antitoxins                                  | 1256 | Diabetic drugs and pharmaceuticals                |
| 1228 | Antivenins (snake venom preparation)        | 1257 | Digestive preparations                            |
| 1229 | Asthma inhalants                            | 1258 | Digitalis stabilization                           |
| 1230 | Astringents                                 | 1259 | Disguising vehicle for bitter medicines           |
| 1231 | Auralodynes and other ear preparations      | 1260 | Disinfectants                                     |
| 1232 | Balsams                                     | 1261 | Diuretic  |
| 1233 | Bentonite pastes                            | 1262 | Douches   |
| 1234 | Bismuth compounds for syphilis              | 1263 | Dry tongue (in fever, etc.)                       |
| 1235 | Bladder treatments                          | 1264 | Dysentery-treating compositions                   |
| 1236 | Blood plasma desiccating cylinders          | 1265 | Eczema preparations                               |
| 1237 | Bone marrow extracts                        | 1266 | Elixirs (other than U.S.P. and N.F.)              |
| 1238 | Botanicals, microscopic identification      | 1267 | Emetics   |
| 1239 | Burn films                                  | 1268 | Emollient and demulcent                           |
| 1240 | Burn jellies and ointments                  | 1269 | Emulsions of tyrothricin, etc.                    |
| 1241 | Burn treatments (with sterile glycerin)     | 1270 | Enemas  |
| 1242 | Callus and corn preparations                | 1271 | Enteric coatings for pills and tablets            |
| 1243 | Cardiac stimulant (spirit of nitroglycerin) | 1272 | Expectorants                                      |
| 1244 | Cataract non-surgical treatment             | 1273 | Eye lotions, drops and washes                     |
| 1245 | Catgut sutures                              | 1274 | First aid material                                |
| 1246 | Chap and chafing compositions               | 1275 | Fissured nipples (e.g., Playfair's solution)      |
| 1247 | Coloring agents                             | 1276 | Flavoring vehicle (e.g., syrups)                  |
| 1248 | Colonic irrigations                         | 1277 | Fluid extracts (other than U.S.P. and N.F.)       |
| 1249 | Compress moistening fluids                  | 1278 | Frost-bite preparations                           |
| 1250 | Compresses (for rheumatism, etc.)           | 1279 | Fungicidal preparations                           |
| 1251 | Contraceptive jellies and creams            | 1280 | Gargles   |
| 1252 | Cough and cold preparations                 | 1281 | Gelatin capsules                                  |
| 1253 | Crust and scab softener                     | 1282 | Glandular extracts                                |
| 1254 | "Cuticolor" preparations                    | 1283 | Glycerin-gelatin combinations (e.g., Unna's boot) |
| 1255 | Dermatological preparations                 | 1284 | Glycerites  |
|      |   | 1285 | Glycero-gelatin casts for ulcers, etc.            |

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|------|---|---|
| 1286 | Glycero-gelatins (other than U.S.P. and N.F.)     | (e.g., cough drops, throat pastilles, etc.)             |
| 1287 | Greaseless bases                                  | 1318 Medicated creams                                   |
| 1288 | Hemoglobin preservation                           | 1319 Medicated dressings                                |
| 1289 | Hemorrhoids injection treatment                   | 1320 Medicated masticatory                              |
| 1290 | Hemostatic solutions                              | 1321 Medicated "paints"                                 |
| 1291 | Hemostatic venoms                                 | 1322 Medicated pastes                                   |
| 1292 | Hernia, injection treatment of                    | 1323 Medicated and surgical soaps                       |
| 1293 | Honey of sodium borate                            | 1324 Mixtures   |
| 1294 | Hormone preparations (as vehicle)                 | 1325 Nasal medicated packs (e.g., ichthyol in glycerin) |
| 1295 | Hydrocele injection treatment                     | 1326 Nasal sprays and drops                             |
| 1296 | Hydrofluoric acid burns                           | 1327 Nasal tampons                                      |
| 1297 | Hyperhydrosis compounds                           | 1328 Neoarsphenamine in glycerin                        |
| 1298 | Ice packs (long lasting)                          | 1329 Non-sensitizing adhesive tapes                     |
| 1299 | Infusions   | 1330 Obstetrical analgesic ("Sigmodal")                 |
| 1300 | Insect bite remedies                              | 1331 Ointment bases                                     |
| 1301 | Instrument disinfectants and sterilizers          | 1332 Osmotherapy  |
| 1302 | Insulin   | 1333 Parasitocides (scabies, etc.)                      |
| 1303 | Intrauterine therapy                              | 1334 Penicillin-producing bandage                       |
| 1304 | Intussusception reduction                         | 1335 Phosphorus burns                                   |
| 1305 | Laxatives   | 1336 Pill manufacture                                   |
| 1306 | Leukoderma and blemish cover compounds            | 1337 Pills of nitroglycerin                             |
| 1307 | Leukorrhea treatments                             | 1338 Plaster bandage                                    |
| 1308 | Liniments   | 1339 Plasters   |
| 1309 | Linseed oil emulsion                              | 1340 Poison gas (mustard) burns-antipruritic ointment   |
| 1310 | Liquid court plaster                              | 1341 Poison gas (Lewisite) neutralizing solution        |
| 1311 | Liver extracts                                    | 1342 Poison-ivy lotions                                 |
| 1312 | Lotions   | 1343 Poultices  |
| 1313 | Lubricating jellies for catheters and instruments | 1344 Promoting water-miscibility of drugs               |
| 1314 | Lymphagogue                                       | 1345 Prosthesis for facial defects                      |
| 1315 | Magmas  |   |
| 1316 | Malaria treatment by injection                    |   |
| 1317 | Medicated confections                             |   |



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|--|---|
| 1346 Pruritus-relieving lotions and creams                             | 1372 Throat paints and solutions  |
| 1347 Renal and uretal calculi treatments                               | 1373 Throat sprays  |
| 1348 Rubbing alcohol compositions and substitutes                      | 1374 Throat swabs   |
| 1349 Sclerosing solutions (varicose therapy, etc.)                     | 1375 Tick (insect) removal  |
| 1350 Sedative preparations   | 1376 Tinctures (other than U.S.P. and N.F.)                               |
| 1351 Serum (immune) conservation                                       | 1377 Tissue-protective ointments  |
| 1352 Silica gels   | 1378 Tonics   |
| 1353 "Slow-epinephrine" preparations                                   | 1379 Trichinosis treatment  |
| 1354 Smelling salts  | 1380 Trichomonas vaginitis treatment                                      |
| 1355 Soluble tar   | 1381 Ulcer pastes and dressings   |
| 1356 Solutions (semi-official)   | 1382 Vaccines   |
| 1357 "Solusalvarsan" injection treatment of syphilis                   | 1383 Vaginal packs  |
| 1358 Solvent for medicinal products and drugs                          | 1384 Vaginal suppositories  |
| 1359 Styptic cotton  | 1385 Vehicle and solvent  |
| 1360 Sulfanilamide solutions (for oral ingestion)                      | 1386 Vitamin vehicles   |
| 1361 Sulfonamide suppositories (vaginal)                               | 1387 War wound antiseptics  |
| 1362 Sulfonamide vehicles (e.g., ointments and creams)                 | 1388 Wart removers  |
| 1363 Sun screen preparations (heliotherapy, ultraviolet therapy, etc.) | 1389 Waterproof dressing covers (Cellophane, artificial oiled silk, etc.) |
| 1364 Surgical drainage   | 1390 Wax (in ear) softening   |
| 1365 Surgical glove sterilization                                      | 1391 Wet dressings and compresses   |
| 1366 Syringe lubricants and storage fluids                             | 1392 Wound dressings  |
| 1367 Syrup substitutes   |   |
| 1368 Tablet manufacture  |   |
| 1369 Tear gas burns of eyes  |   |
| 1370 Thermometers, rectal (facilitates use)                            |   |
| 1371 Thioglycerol in glycerin  |   |
- 
- | <b>Foods</b> |  |
|--------------|--|
| 1393         | Anti-graining agent in baking, candy making, etc.  |
| 1394         | Artificial chewing gum bases (modified ester gums) |
| 1395         | Artificial essences and ethers                     |
| 1396         | Baked goods  |
| 1397         | Brazil nuts flavor and moisture retention          |
| 1398         | Bread dough improver                               |

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|------|--|------|--|
| 1399 | Bread preservation                                   | 1433 | Immersion quick-freezing processes           |
| 1400 | Cheeses, processed                                   | 1434 | Infant foods                                 |
| 1401 | Chewing gum  | 1435 | Inks for food packaging                      |
| 1402 | Chocolate bars resistant to hot weather              | 1436 | Jellies and jams                             |
| 1403 | Chocolate manufacture                                | 1437 | Licorice compounds                           |
| 1404 | Coconut preservation                                 | 1438 | Lubricant for food-processing equipment      |
| 1405 | Cod-liver-oil emulsions                              | 1439 | Malt extracts                                |
| 1406 | Coloring compositions                                | 1440 | Margarine emulsifiers                        |
| 1407 | Confectionery  | 1441 | Marshmallow                                  |
| 1408 | Culinary ingredient                                  | 1442 | Meat casings                                 |
| 1409 | Curdling prevention for custards                     | 1443 | Meat extracts                                |
| 1410 | Curing salts for meats                               | 1444 | Meat-seasoning compounds                     |
| 1411 | Dehydrated foods                                     | 1445 | Meat-stamping inks                           |
| 1412 | Diabetic foods                                       | 1446 | Milk-specimen preservative                   |
| 1413 | Dried fruit treatments                               | 1447 | Milk testing                                 |
| 1414 | Edible fats  | 1448 | Modifying natural oils                       |
| 1415 | Egg and egg yolk processing                          | 1449 | Nutrient                                     |
| 1416 | Emulsifiers  | 1450 | Nut-skinning solutions                       |
| 1417 | Emulsifiers for general food uses                    | 1451 | Odor-development inhibitor                   |
| 1418 | Flavoring compositions                               | 1452 | Packaging materials                          |
| 1419 | Flavor pastes and emulsions                          | 1453 | Peanut-butter improver                       |
| 1420 | Food analysis  | 1454 | Pectin extraction and preservation           |
| 1421 | Fowl-plucking composition (ester gum)                | 1455 | Preserves (whole fruit, etc.)                |
| 1422 | Freezing-point depressant for ice cream, etc., mixes | 1456 | Preservatives for food products              |
| 1423 | Freshness retention                                  | 1457 | Preserving cut surfaces of fresh meat        |
| 1424 | Frozen food containers and packagings                | 1458 | Preventing milk boiling over                 |
| 1425 | Frozen foods indicator inks                          | 1459 | Protective coatings for fruits, nuts, etc.   |
| 1426 | Fruit cakes  | 1460 | Protective coatings on meats, poultry, etc.  |
| 1427 | Fruit juice preservation                             | 1461 | Protectives against poison gases             |
| 1428 | Gelatin products                                     | 1462 | Rancidity preventive in dairy products, etc. |
| 1429 | Glazes for frozen foods                              |      |  |
| 1430 | Glycero-gelatin bases for jellies, jujubes, etc.     |      |  |
| 1431 | Ice-cream manufacture                                |      |  |
| 1432 | Icings and frostings for cakes                       |      |  |

1463	Rennet preparation and preservation		<b>Tobacco</b>
1464	Rice oil purification	1491	Casing mixtures
1465	Shortenings	1492	Chewing-tobacco treatments
1466	"Smoked" flavor coatings	1493	Cigarette papers (special)
1467	Solid seasoning compositions	1494	Crumb-formation prevention
1468	Soy-bean products	1495	Facilitating tobacco handling
1469	Special foods for invalids	1496	Flavor solvent
1470	Stabilizers for food emulsions	1497	Humectant (for moisture retention)
1471	Sterilizer for foods	1498	Humidifier
1472	Sugar refractometer standardization	1499	Mold inhibition
1473	Sweetening agent	1500	Packaging materials
1474	Synthetic fats	1501	Plumping agent for cigarettes
1475	Tallowy-odor retarder for grain products	1502	Scrap tobacco salvage
1476	Treating teaseed oil	1503	Smoking irritation reducer
1477	Vegetable extracts	1504	Tobacco humidors
1478	Yeast products	1505	Tobacco improvers

**Perfumes**

1479	Aromatic chemicals (derivatives)
1480	Cologne waters
1481	Eau de Quinine
1482	Emulsion perfumes and colognes
1483	Extractant for odorous constituents of flowers
1484	"Fixative" for perfumes
1485	Glycerin derivative fixatives (e.g., glyceryl acetate)
1486	Perfume extractive (derivative)
1487	"Solid" perfumes
1488	Solvent
1489	Toilet waters
1490	Vehicle and sterilizer in perfumes

**Veterinary Medicine**

1506	Animal liquid soaps
1507	Antiseptic solutions
1508	Antiseptic wash for genital horse pox
1509	Bird colas
1510	Bird tonics
1511	Blow-fly "strike" prophylaxis and treatment
1512	Calf scour prevention
1513	Catarrhal otorrhea therapy
1514	Chicken-pox treatment
1515	Cough electuary for horses
1516	Cracked-heel treatment for horses
1517	Dermatological preparations
1518	Disinfectants
1519	Dog mouth wash



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|------|---|------|--|
| 1577 | Preserving botanical,<br>zoological and ana-<br>tomical specimens | 1580 | Poison gas indicators                  |
| 1578 | Preserving decorative<br>foliage                                  | 1581 | Skin protection against<br>mustard gas |
| 1579 | Preserving flowers  | 1582 | Tattoo mark removal                    |
|      |   | 1583 | Telephone mouthpiece<br>antiseptic     |



# APPENDIX

## TABLES SHOWING PROPERTIES OF GLYCERIN

THE TABLE and charts reproduced in the following pages are included primarily for the benefit of the chemist or technician who may need this precise assistance in determining the reaction of glycerin in application to specific research problems.

When water and glycerin are mixed, a slight amount of heat is given off and the volume contracts slightly. When there is a relatively small amount of water, the vapor pressure curve lies below the diagonal.

It will be noted that the viscosity of glycerin at various temperatures increases rapidly beyond 60-70% concentration.

For the quantitative estimation of small amounts of water in glycerin, the freezing point method is convenient and accurate.

### Aqueous Glycerin Solutions \*

#### Apparent Specific Gravity (Air)

% Glycerol	25/25°C.	% Glycerol	25/25°C
100	1.26201	50	1.12720
99	1.25945	49	1.12450
98	1.25685	48	1.12185
97	1.25425	47	1.11915
96	1.25165	46	1.11650
95	1.24910	45	1.11380
94	1.24645	44	1.11115
93	1.24380	43	1.10845
92	1.24115	42	1.10575
91	1.23850	41	1.10310
90	1.23585	40	1.10040
89	1.23320	39	1.09775
88	1.23055	38	1.09510
87	1.22790	37	1.09245
86	1.22520	36	1.08980
85	1.22255	35	1.08715
84	1.21990	34	1.08455
83	1.21720	33	1.08190
82	1.21455	32	1.07925

Aqueous Glycerin Solutions \* (*Continued*)

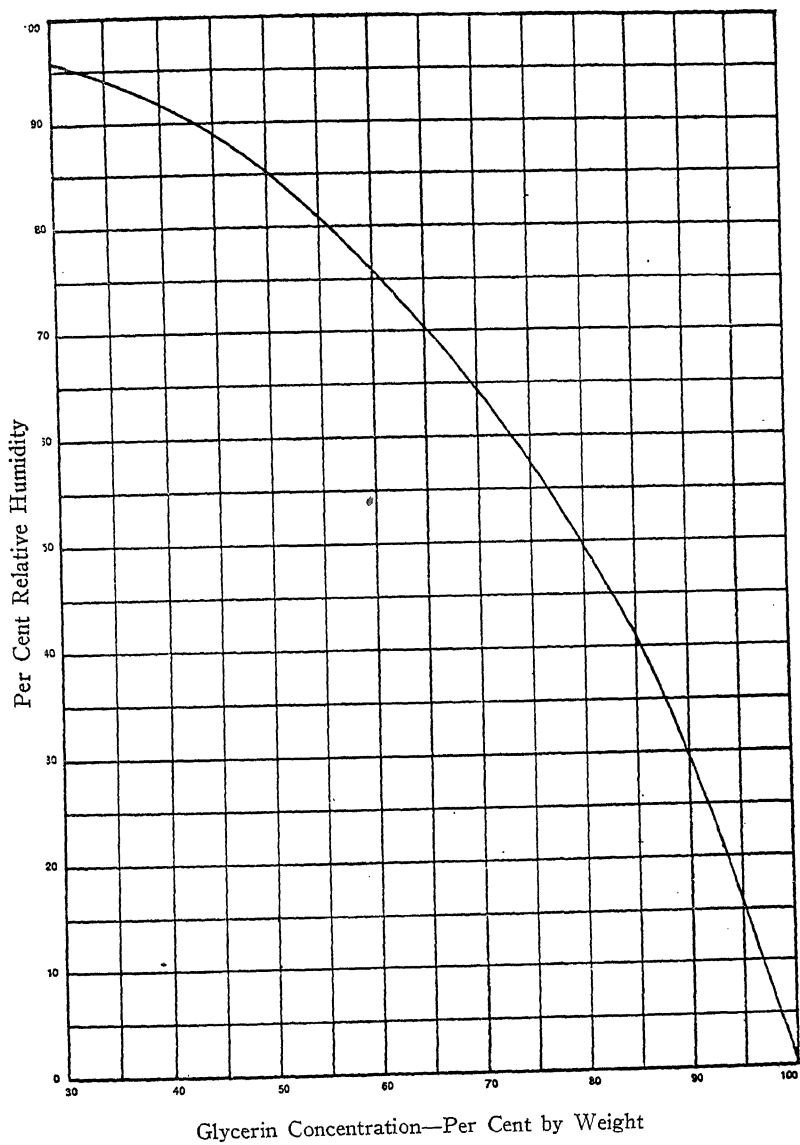
Apparent Specific Gravity (Air)

% Glycerol	25/25°C.	% Glycerol	25/25°C
81	1.21190	31	1.07660
80	1.20925	30	1.07395
79	1.20655	29	1.07135
78	1.20380	28	1.06880
77	1.20110	27	1.06625
76	1.19840	26	1.06370
75	1.19565	25	1.06115
74	1.19295	24	1.05860
73	1.19025	23	1.05605
72	1.18755	22	1.05350
71	1.18480	21	1.05095
70	1.18210	20	1.04840
69	1.17935	19	1.04590
68	1.17660	18	1.04345
67	1.17385	17	1.04100
66	1.17110	16	1.03850
65	1.16835	15	1.03605
64	1.16560	14	1.03360
63	1.16285	13	1.03110
62	1.16010	12	1.02865
61	1.15735	11	1.02620
60	1.15460	10	1.02370
59	1.15185	9	1.02135
58	1.14915	8	1.01900
57	1.14640	7	1.01660
56	1.14365	6	1.01425
55	1.14090	5	1.01185
54	1.13815	4	1.00950
53	1.13540	3	1.00710
52	1.13265	2	1.00475
51	1.12995	1	1.00235

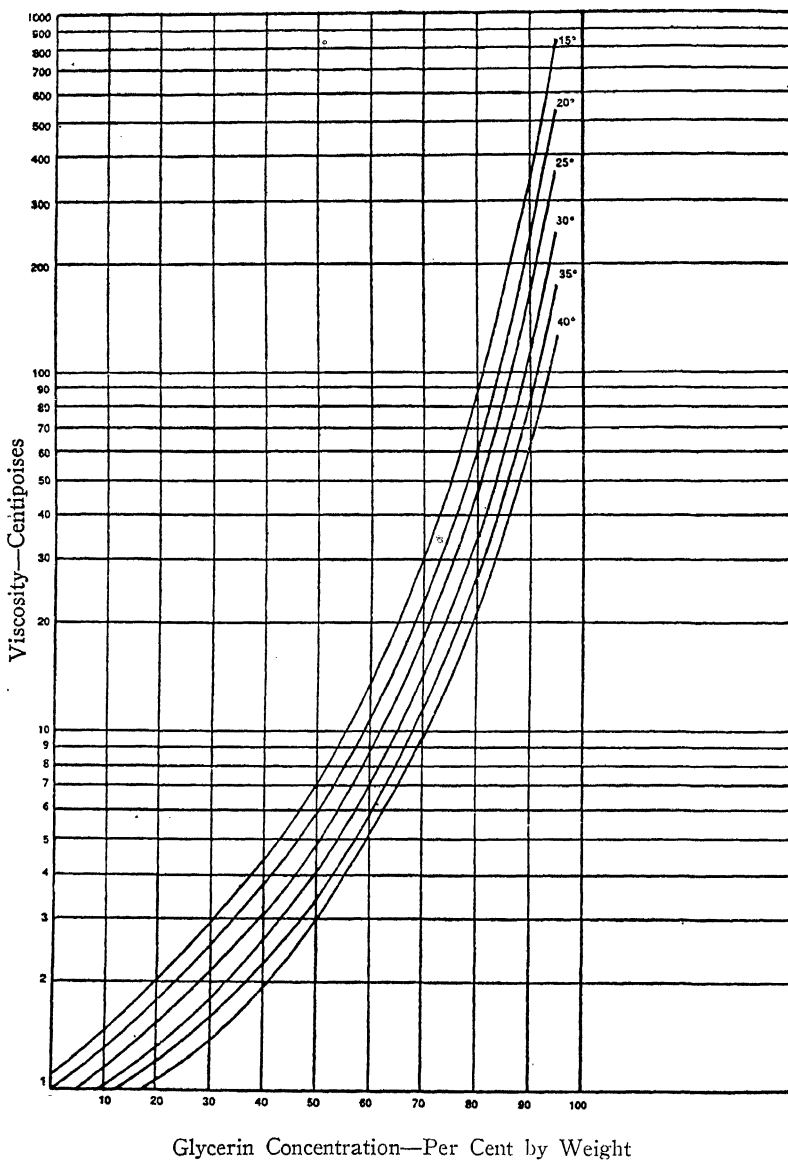
\* Courtesy of Bosart & Snoddy, *Ind. Eng. Chem.*, 19, 506 (1927).



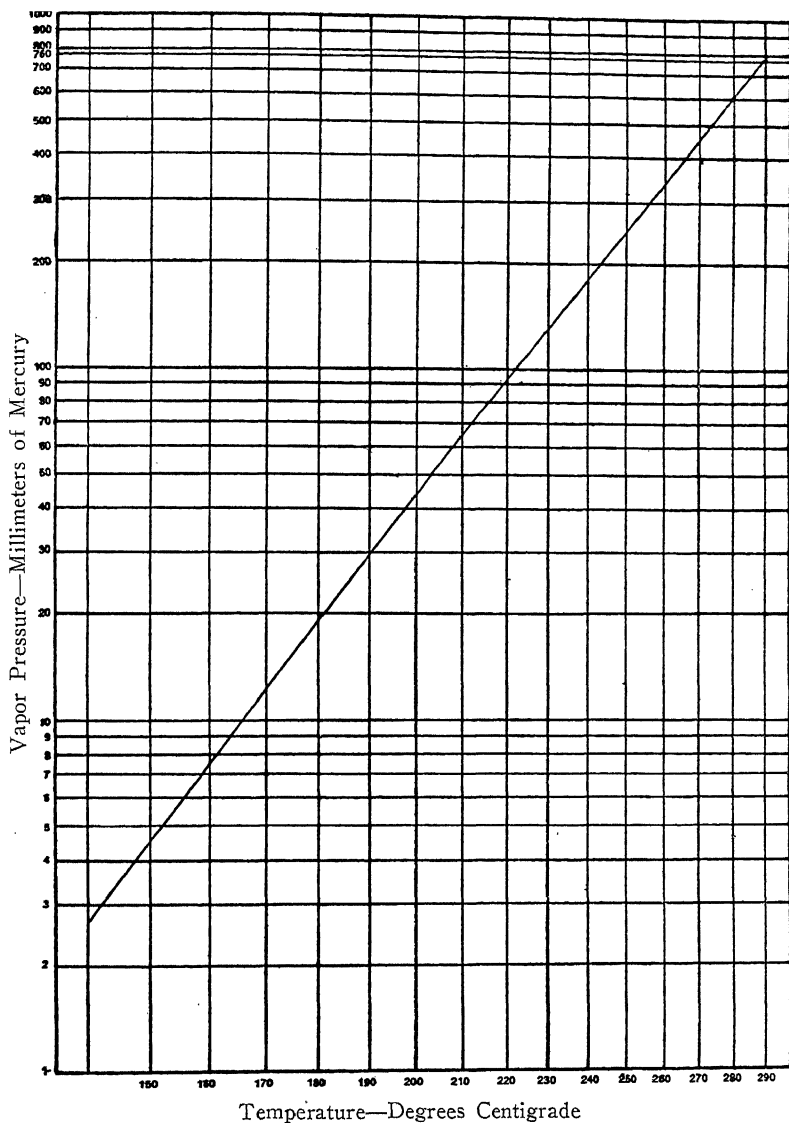
Relative Humidity Over Aqueous Glycerin Solutions  
15-45° Centigrade



Glycerin Concentration Against Viscosity at 15 to 40°C.

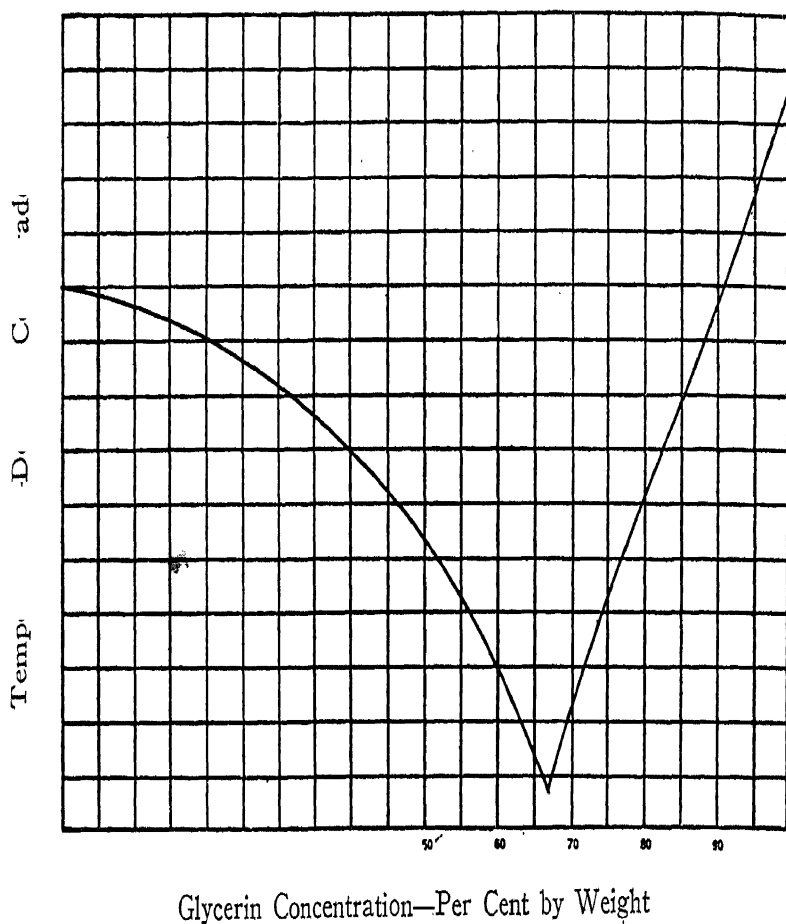


## Vapor Pressure of Glycerin Against Temperature \*



Printed by permission, J. W. Lawrie, *Glycerol and the Glycols*, p. 176,  
Reinhold Publishing Corp., 1942.

Freezing Point Diagram for Glycerin-Water Solutions\*



\* Courtesy of L. B. Lane, *Ind. Eng. Chem.*, 17, 924 (1925).

# INDEX

- Abels, Sir Frederick, 34
- Abrasive composition, 192
- dental cleansing, 169
- glass grinding, 192
- mixture, dental laboratory, 172
- sheet, 84
- Acid cream, 138
- Acne cream, 134
- Adherence grease, strong, 43
- Adhesive, Cellophane, 12, 63
- cloth laminating, 107
- fibrous material, 67
- glass, 120
- label, 9, 10
- laminated container, 60
- light-sensitive emulsion, 72
- metal, 67
- mounting, 78
- packaging, 13
- paper-to-glass, 10
- remoistening, 11, 12
- tin can, 11
- Adhesives, 8
- Adulteration, butter, Grossfeld's test  
for, 152
- wine, 145
- Afterbirth wash, retained, 187
- After-shave lotion, 137
- Agriculture, 124
- Aircraft finish, 82
- Alcohol-glycerin rennet, 151
- Alkaline mouth wash, 165
- Alkyd resin, 27, 73, 81, 82, 95, 98, 108,  
109, 119, 174, 193
- resins, classification of, 97
- resins, history of, 96
- resins, manufacturers of, 98
- resins, production of, 97
- resins, properties of, 96
- Allergy preparation, glycerin in, 180
- Aluminum cleaner, 20
- electrolytic treatment of, 27
- etching solution, 56
- polish, 20
- Ammonia gelatin dynamite, 33
- Angina treatment, Vincent's, 165
- Animal dip. *See* Sheep dip.
- Animal ear therapy, 162
- ear trouble mixture, 186
- eyewash, 186
- fats, 2
- wound treatment, 186
- Anti-curl solution, 77
- Anti-dryness inhalant spray, 181
- Anti-fog glass, 119
- Antigen, 157
- Antiparasitic lotion, 184
- Antipruritic lotion, 184
- Antiseptic, 160, 183
- dental, 164
- mouth, 169
- "Anti-stick" agent, 101
- Application of sulfonamides, topical,  
glycerin in, 167, 177
- Aqueous emulsion of coal-tar oil, 43
- emulsion of mineral oil, 43
- Artificial denture polish, 172
- fruit essence, 143
- Asthmatic inhalant spray, 181
- Astringent, 135
- eye lotion, 196
- "Athlete's foot" mixture, 181

## B

- Bait preparation, bran, 126
- Ballistite, 32, 34
- Base, liqueur flavor, 146
- matt skin cream, 132
- powder, 136
- Batteries, electric, 28
- Beater size, 69
- Bed sore treatment, 160
- Berzelius, 96
- Beverage preservative, 140
- Beverages, 140
- Binding agent, 25, 29, 72, 84
- Black dressing, brilliant, 39
- varnish, dead, 77
- Blanket, printing, 88, 91

- Blasting gelatin, 33
- Bleaching bath, 74
- Blow-fly strike preventative, 184
  - strike treatment, 184
- Bowman's solution, 166
- Bran bait preparation, 126
- Brilliant black dressing, 39
- Brilliantine, 137
- Bromide paper developer, 75
- Burn Fluid 19, 178
  - Fluid 20, 179
  - preparation, 179
  - treatment, glycerin in, 158, 159
- Burn-treating products, sulfonamide, 178
- Butter adulteration, Grossfeld's test for, 152
  
- Cadmium plating, 26
- Calamine cream, 134
- Camera coating, glycerin as, 72
- Canal filling paste, 168
  - preparation, root, 167
- Canker wash, pear-tree, 125
- Can-sealing composition, 12
- "Carbolic and Glycerine" sheep dip, 190
- Carrier, emulsion, 73
- Casing, meat, 41, 154
  - mixture, cigarette, 114
- Cast, mold for duplicating plaster, 170
- Catalyst, 3
- Cattle feed, 130
  - ringworm treatment, 183
- Cellophane adhesive, 12, 63
  - glycerin content of, 61
  - manufacture, glycerin in, 12, 61
- Cellulosic film, 73
- Cement, electrical conducting, 29
  - glycerin-litharge, 120
  - metal-glass, 120
- Cements, 8
- Cheese manufacture, 151
- Chemical properties of glycerin, 5
  - reactivity of glycerin, 5
- Chemically pure glycerin, 3
- Chester's formaldehyde-glycerin wash, 124
- Children, disclosing solution for, 168
- Chocolate essence, 144
- Cigarette casing mixture, 114
- Classification of alkyl resins, 97
- Cleaner, aluminum, 20
  - glass, 19
  - magnesium, 19, 54
  - magnesium-base alloy, 19, 54
  - metal, 19
  - spectacle, 194
- Cleaners, 15
- Cleaning cloth, metal, 18
- Cleansing abrasive, dental, 169
  - pad, cosmetic, 137
- Cloth laminating adhesive, 107
  - spectacle polishing, 194
- Coal-tar oil, aqueous emulsion of, 43
- Coated roller, 90
- Coating for food, protective, inedible, 151
  - for leather, waterproof, 40
  - glass, 84
  - glycerin as camera, 72
  - glycerin as plate holder, 72
  - grease-resisting, 66
  - protective, 82
  - rubber surface, 100
  - synthetic, 82
  - synthetic rubber, 110
  - textile, 84, 108
- Coatings, protective, 95
- Cod liver oil emulsion, 188
- Cold drawing metal lubricant, 47
- Collotype process, 92
- Color photography, 73, 74
  - photography film, 84
- Coloring, food, 144, 152
  - textile, 84
- Composite container, sealing composition for, 12, 13
- Composition, dental imprint, 170
  - plastic, 84
  - roller, 88
- Compound vanilla extract, 142
- Condensers, electrolytic, 23
- Conservation, rubber, 102
- Consumption of glycerin by the tobacco industry, 112
  - of glycerin in food, annual, 2
- Container adhesive, laminated, 60
  - sealing composition, 84
  - sealing composition, food, 100
- Contents, v
- Copper-tempering solution, 172

Cordite, 32, 34  
Corrosion inhibiting agent, 52  
Cosmetic cleansing pad, 137  
—stockings, 133, 135, 136  
Cosmetics, 131  
Cough electuary, horse, 187  
Cream, acid, 138  
—acne, 134  
—base, matt skin, 132  
—calamine, 134  
—day, 133  
—stocking-simulating, 133  
Crown and plate swager, elastic compound for, 170  
Crude glycerin, 3  
Cup grease, glycerin in, 43  
Curing, meat, 154

## D

Day cream, 133  
Dead black varnish, 77  
Demulcent, 157  
Demulsifying agent, 44  
Dental antiseptic, 164  
—cleansing abrasive, 169  
—disclosing solution, 168  
—disclosing solution for children, 168  
—impression wax, 169  
—imprint composition, 170  
—laboratory abrasive mixture, 172  
—molding press lubricant, 171  
—polishing agent, 172  
—solution, preoperative, 164  
—thermoplastic molding composition, 171  
—wax lubricant, 171  
Dentistry, 164  
Denture polish, artificial, 172  
Deodorant, 135  
Depressant, freezing point, 145, 150, 152  
Derivatives, glycerol, 198  
Dermatology, glycerin in, 159, 160  
Desalting agent, 44  
Destroyer, pest, 124  
Developer, bromide paper, 75  
—for platinum paper prints, 75  
—preservative, glycerin as, 74  
Developing bath, 74  
Dewaxing agent, 44  
Diaphragms, sound, 79  
Diazotype film, 72  
Diazotype paper, 72  
Diet, glycerin in, 2  
Dip, sheep, 128, 190  
Direct color photography, glycerin in, 71  
Discharge tube, 23, 24, 25, 27  
Disclosing solution, dental, 168  
—solution for children, dental, 168  
Dispersing agent, insecticide, 125  
Dog "hair restorer" lotion, 184  
—mouthwash, 188  
—shampoo, 185  
—wash, 185  
Dog's foot treatment, 130, 187  
Double base powders, 34  
Dressing, brilliant black, 39  
—"glycerin-diboric," 184  
—leather, 38  
—penicillin, 180  
Dry socket prevention, 167  
Dryer, 76  
Duplicating plaster cast, mold for, 170  
Dyes, 105  
Dynamite, 32  
—ammonia gelatin, 33  
—consumption in the United States, 32  
—gelatin, 33  
—glycerin, 3  
—strength of, 32  
Ear mange preparation, 129, 185  
—mange preparation, fox, 185  
—mange preparation, rabbit, 185  
—therapy, animal, 162  
—trouble mixture, animal, 129, 186  
Earwig destroyer, 126  
Eczema lotion, moist, 184  
Edible glycerin. *See* Chemically pure glycerin.  
Eggs, glycerin in, 149  
Elastic composition, 103  
—compound for crown and plate swager, 170  
Electric batteries, 28  
Electrical conducting cement, 29  
—equipment, 23  
—insulating cambric, 109  
—static prevention, 93

- Electrode, graphite, 26  
 Electrodeposition, 23, 26  
   — of tungsten alloys, 50  
 Electrolytic condenser, 23  
   — steel polish, 51  
   — treatment of aluminum, 27  
 Electroplating, 26, 50  
   — plasticizer in, 26  
 Electuary, horse cough, 187  
 Emollient, 157, 183  
 Emulsifying agent, insecticide, 125  
   — agent, margarine, 152  
 Emulsion base, oil-in-water, 177  
   — carrier, 73  
   — paint. *See* Water paint.  
 Emulsions, glycerin in, 132  
 Emulsion-type furniture polish, 15, 16  
 Enamel, 83  
 Enema, 161  
   — "two-four-six," 161  
 Epichlorohydrin, 204  
 Equipment, electrical, 23  
 Essence, artificial fruit, 143  
   — chocolate, 144  
 Etching compound, glass, 119  
   — printing plate, 92  
   — solution, aluminum, 56  
   — solution, stainless steel, 56  
   — solution, tin plate, 56  
   — solution, white metal, 56  
 Explosionproof lubricant, 46  
 Explosives, 31  
   — permissible, 33  
 Exterminator, fly, 126  
 Extract, compound vanilla, 142  
   — vanilla, 142  
   — vanilla, non-alcoholic, 142  
 Eye lotion, 195, 196  
   — lotion, astringent, 196  
   — preparation preservative, 196  
 Eyewash, animal, 186  
  
 Fats, saponification of, 2  
 Fatty acids, 3  
 Favus treatment, poultry, 188  
 Feed, cattle, 130  
 Fermentation, glycerin from wine, 2  
 Fertilizing mixture, 130  
 Fibrous material adhesive, 67  
  
 Field mouse poison, 127  
 Filling paste, canal, 168  
 Film, cellulosic, 73  
   — color photography, 84  
   — diazotype, 72  
   — protecting paper, 79  
   — sulfa, 178  
 Finger tip moistener, printer's, 93  
 Finish, aircraft, 82  
   — alkyd-resin, 82  
   — for kid leather, gum lac casein, 39  
   — specification, 82  
   — synthetic rubber, 99, 100  
 Finishing agent, leather, 38  
 Fire hazard, 9  
 Fixing bath, 74  
 Flameproofing agent, 60, 62  
 Flavor base, liqueur, 146  
 Flavoring composition, scrap-tobacco, 116  
   — paste, 142  
   — powdered, 142  
 Flexibilizer. *See* Plasticizer.  
 Fluid, soldering, 54  
 Fluid-sealing material, 101  
 Flux, soldering, 55  
 Fly exterminator, 126  
   — spray, 126, 127  
 Foam-producing liquid, 145  
 Food coloring, 144, 152  
   — container sealing composition, 100  
   — freezing, 154  
   — packaging, 154  
   — preservation from war gases, 63, 108  
   — processing preservative, 149, 154  
 Foods, 149  
   — containing glycerin, 2  
 Foot treatment, dog's, 130, 187  
 Forge scale remover, 53  
 Formaldehyde-glycerin wash, Chester's, 124  
 Formalin hardening bath, 76  
 Formula of glycerin, 1  
 Foundation, make-up, 136  
 Fowl tonic pills, 189  
 Fox ear mange preparation, 185  
 Freezing, food, 154  
   — point depressant, 145, 150, 152  
 Fresh fruit syrup, 144  
 "Frozen" syringe, 161



- Fruit essence, artificial, 143
- syrup, fresh, 144
- Fumigating insecticide, 127
- Function of glycerin in medicinals, 158
- Furniture polish, 16, 17
- polish, emulsion-type, 15, 16
  
- Galvanizing, glycerin in, 55
- Gasoline pump grease, 44, 45
- Gas-resistant fabrics, 108
- Gelatin, blasting, 33
- dynamite, 33
- negative stripping solution, 78
- products, 153
- Germination, seed, 124
- Gin, Holland, 147
- Gingivitis treatment, 165
- Glass, 119
- adhesive, 120
- anti-fog, 119
- anti-mist, 119
- cleaner, 19
- coating, 84
- etching compound, 119
- grinding abrasive, 192
- laminating agent, safety, 119, 120, 195
- mucilage, 193
- polish, 119, 192
- safety, 119
- Glass-marking ink, 119, 193
- Glass-to-metal cement, 120
- Glass-to-paper adhesive, 10
- Glossy paper emulsion, 73
- Glue, non-warps, 9
- paper box, 9
- Glue-glycerin composition, 88, 89
- Glycerides, 2
- Glycerin derivatives, 198
- formal, 209
- furfural, 210
- pencil, 195
- "process," 74
- suppository, 161
- "Glycerin-diboric" dressing, 184
- Glycerin-iodine solution, 168
- Glycerin-litharge cement, 120
- Glyceryl  $\alpha$ ,  $\gamma$ -dichlorohydrin, 203
- $\alpha$ ,  $\gamma$ -diisoamyl ether, 208
- $\alpha$ ,  $\gamma$ -dimethyl ether, 207
- Glyceryl  $\alpha$ ,  $\gamma$ -diphenyl ether, 208
- laurate S, 201
- $\alpha$ -mono-n-butyl ether, 205
- $\alpha$ -monochlorohydrin, 203
- $\alpha$ -monoisoamyl ether, 206
- $\alpha$ -monomethyl ether, 205
- $\alpha$ -monophenyl ether, 207
- monoricinoleate S, 201
- monostearate S, 202
- Glyceryltrinitrate. *See* Nitroglycerin.
- Glyptal resin. *See* Alkyd resin.
- Gold from silver stripping, 51
- polish, 21
- Grades of glycerin, 3
- Graphite electrode, 26
- Grease, gasoline pump, 44, 45
- lime base, 43
- strong adherence, 43
- Greaseless hair pomade, 132
- Greaseproofing agent, 59, 65, 68
- Grease-resistant coating, 66
- Greenhouse insecticide, 127
- Grinding abrasive, glass, 192
- Grossfeld's test for butter adulteration, 152
- Gum, label. *See* Label adhesive.
- Gum lac casein finish for kid leather, 39
  
- H
  
- Hair cream, non-greasy, 137
- pomade, greaseless, 132
- pomade, pectin, 133
- restoring lotion, dog, 184
- Hardening bath, formalin, 76
- Heading liquid, 145
- Hide preservative, 36
- softening agent, 37, 38
- High-gravity glycerin, 3
- High-temperature lubricant, 48
- History of alkyd resins, 96
- of glycerin, brief, 1
- "Hock-curb" treatment, 186, 187
- Holland gin, 147
- Horse cough electuary, 187
- physic balls, 187
- Hose preserving composition, 107
- Hygroscopic agent, 3, 8, 113, 114, 115, 116, 117
- Hypo-glycerin photographic stain remover, 78

- Ice cream, low carbohydrate, 150
- cream mix, 150
- Imbedding medium, glycerin as, 68
- Impression wax, dental, 169
- Imprint composition, dental, 170
- Industrial glycerin, 3
- Inedible protective coating, 151
- Infection, tree, 125
- Inhalant spray, anti-dryness, 181
- spray, asthmatic, 181
- Ink, glass-marking, 119, 193
- printing, 84, 88, 93
- Insect-destroying preparation, 125
- Insecticidal spray, 125
- Insecticide dispersing agent, 125
- emulsifying agent, 125
- fumigating, 127
- greenhouse, 127
- vaporizing, 127
- Instrument lubricant, medical, 161, 162
- Insulating agent, 23, 28, 84
- Iodine solution for Vincent's angina, 166
- Iodine-glycerin solution, Talbot's, 164, 165
- Jam preparation, 153
- K
- Kellner, Dr. W., 34
- Kid leather, gum lac casein finish for, 39
- Leather, gum lac casein finish for kid, 39
- sole, 40
- Light-sensitive emulsion adhesive, 72
- Lime base grease, 43
- Liqueur flavor base, 146
- Liquid powder, 134
- Lithography, 88
- Lotion, after-shave, 137
- antiparasitic, 184
- antipruritic, 184
- astringent eye, 196
- dog "hair restorer," 184
- eye, 196
- moist eczema, 184
- Low carbohydrate ice cream, 150
- temperature lubricant, 45
- Lubricant, cold drawing metal, 47
- dental molding press, 171
- dental wax, 171
- explosionproof, 46
- gasoline pump. *See* Gasoline pump grease.
- high temperature, 48
- insoluble in organic solvents, 45
- low temperature, 45
- medical instrument, 161, 162
- molding press, 47
- non-greasy, 47
- pipe thread, 47
- rubber, 46
- rubber surface, 101, 102
- synthetic resin, 48
- Lubricants, 42
- glycerin in petroleum, 44
- Luster restoration, 106
- M
- Machine oil, 44, 172
- Magnesium cleaner, 19, 54
- Magnesium-base alloy cleaner, 19, 54
- Make-up foundation, 136
- Mange preparation, ear, 129, 185
- preparation, fox ear, 185
- preparation, rabbit ear, 185
- treatment, sarcoptic, 185
- Manufacturers of alkyd resins, 98
- Margarine emulsifier, 152
- Masking paste, 76
- Materials, packaging, 58
- Matrix, printing, 88, 92
- Matt skin cream base, 132
- Label adhesive, 9, 10
- for metal surface, moistening fluid for, 11
- paste for lithographed cans, 11
- Laminated container adhesive, 60
- Laminating adhesive, cloth, 107
- agent, 84
- agent, safety glass, 119, 120, 195
- Leather, 36
- coating, waterproof, 40
- dressing, 38
- finishing agent, 38

Matte paper emulsion, 73  
 Meat casing, 41, 154  
   — curing, 154  
 Medical instrument lubricant, 161, 162  
 Medicinals, function of glycerin in, 158  
 Medicine, 157  
   — veterinary, 183  
 Metal adhesive, 67  
   — cleaner, 19  
   — cleaning cloth, 18  
   — etching solution, white, 56  
   — lubricant, cold drawing, 47  
   — polish, 17, 18  
   — polishing cloth, 18  
   — surface, moistening fluid for  
     gummed label for, 11  
 Metal-glass cement, 120  
 Metals, 50  
 Milk product preservation, 151  
 Mineral oil, aqueous emulsion of, 43  
 Mixture, dental abrasive, 172  
 Moist eczema lotion, 184  
 Moistener, printer's finger tip, 93  
 Moistening fluid for gummed label  
   for metal surface, 11  
 Moisture absorption. *See* Hygroscopic  
   agent.  
 Mold for duplicating plaster cast, 170  
 Moldine, 170  
 Molding, 54, 83, 85, 170  
   — composition, dental thermoplastic,  
     171  
   — press lubricant, 47  
   — press lubricant, dental, 171  
   — sand, 171  
 Mountant, 68, 190  
 Mounting adhesive, 78  
 Mouse poison, field, 127  
 Mouth antiseptic, 169  
   — treatment, trench, 165  
   — wash, 169  
   — wash, alkaline, 165  
   — wash, dog, 188  
   — wash, oxidizing, 165  
   — wash, stomatitis, 166  
 Mucilage, glass, 193

## N

Napkin softening agent, paper, 66  
 Negative, photographic paper, 79  
   — stripping solution, gelatin, 78

Nickel plating bath, 26  
   — stripping, from steel, 51  
 Nitroglycerin, 31  
   — history of, 31  
 Nobel, Alfred, 31  
 Non-alcoholic vanilla extract, 142  
 Non-greasy hair cream, 137  
   — lubricant, 47  
 Non-ionic surface-active agent, 198  
 "Non-meltable" roller, 90  
 Non-toxicity of glycerin, 131, 141  
 Non-warp glue, 9  
 Nursing, glycerin in, 161

## O

Offset cure, 93  
 Oil, machine, 44, 172  
   — resistant softener, 60, 69  
 Oil-in-water emulsion base, 177  
 Oils, saponification of, 2  
 Olive oil, glycerin from, 2  
 Optometry, 192  
 Orthodontia, 164  
 Oxidizing mouth wash, 165

Packaging adhesive, 13  
   — food, 154  
   — materials, 58  
 Paint, water, 83, 98  
 Paints, 95  
 Paper, 65  
   — box glue, 9  
   — diazotype, 72  
   — emulsion matte, 73  
   — film protecting, 79  
   — glossy emulsion, 73  
   — napkin softening agent, 66  
   — sizing agent, 66  
   — softener, 65  
   — towel softening agent, 66  
 Paper-impregnating material, 115  
 Paper-proofing composition, 67  
 Paper-to-glass adhesive, 10  
 Parasiticide, 183  
 Partial glyceryl ester, 198  
 Paste, canal filling, 168  
   — flavoring, 142  
   — masking, 76  
   — printing, 88, 93, 105  
   — spectacle, 194

- Pear-tree canker wash, 125  
Pectin hair pomade, 133  
— preparation, 153  
Pencil, glycerin, 195  
Penetrating properties of glycerin, 8  
Penicillin dressing, 180  
Permissible explosives, 33  
Pest destroyer, 124  
Pest-resisting agent, 67  
Petroleum lubricants, glycerin in, 44  
Pharmaceutical properties of glycerin, 176  
Pharmaceuticals, 176  
— function of glycerin in, 158  
Photo gelatin printing process, 88, 92  
Photographic emulsions, 71  
— paper negatives, 79  
— plate softening agent, 72  
— restrainer, glycerin as, 74  
— stain remover, hypo-glycerin, 78  
Photography, 71, 78  
— color, 71, 73, 74  
— color film, 84  
Physic balls, horse, 187  
Physical properties of glycerin, 244  
Physiology of glycerin, 157  
Pigeon tonic, 189  
Pipe thread lubricant, 47  
Plaster cast, mold for duplicating, 170  
Plastic composition, 84  
— shortening, 150  
Plasticizer, glycerin as, 8, 26, 58, 63, 65, 71, 81, 85, 99, 107, 120, 172, 178, 193  
— polyvinyl alcohol resin, 101  
— synthetic fiber, 108  
Plastics, 81  
Plate and crown swager, elastic compound for, 170  
— etching, printing, 92  
— etching solution, tin, 56  
— holder coating, glycerin as, 72  
— printing, 88, 92  
Plating bath, nickel, 26  
— cadmium, 26  
Platinum paper prints, developer for, 75  
Poison, field mouse, 127  
— rat, 127  
Polish, aluminum, 20  
— artificial denture, 172  
— furniture, 16, 17  
— Polish, glass, 119, 192  
— gold, 21  
— metal, 17, 18  
— silver, 20  
— steel electrolytic, 51  
— stove, 21  
Polishes, 15  
Polishing cloth, metal, 18  
— cloth, silver, 20  
— cloth, spectacle, 194  
Polyvinyl resin plasticizer, 101  
Pomade, greaseless hair, 132  
— pectin hair, 133  
Poultry favus treatment, 188  
Powder base, 136  
— double base, 34  
— flavoring, 142  
— liquid, 134  
— smokeless, 32, 35  
Preface, iii  
Preoperative dental solution, 164  
Prescriptions, glycerin in, 157  
Preservative, beverage, 140  
— developer, 74  
— eye preparation, 196  
— glycerin as a, 4  
— hide, 36  
— hose, 107  
— in food processing, 149, 154  
— milk product, 151  
— specimen, 190  
— vulcanized rubber, 173  
Preserve preparation, 153  
Pretanning preparation, 36  
Print transfer, 79  
— varnish, 77  
Printer's finger tip moistener, 93  
— roller composition, 90  
Printing, 88  
— blanket, 88, 91  
— ink, 84, 88, 93  
— matrix, 88, 92  
— paste, 88, 93, 105  
— plate, 88, 92  
— plate etching, 92  
— process, photo gelatin, 88, 92  
— roller. *See* composition roller.  
— screen, 93, 105  
Prints, platinum paper, developer for, 75  
Production of alkyd resin, 97  
Projection screen, 79

- Properties of glycerin, 1, 4, 15  
— of glycerin, chemical, 5  
— of glycerin, pharmaceutical, 176  
— of glycerin, physical, 244  
Protecting paper, film, 79  
Protective coating, inedible food, 151  
— coatings, 82, 95  
Purification of glycerin, 2  
Pyorrhea treatment, 164
- Q
- Quenching agent, 52
- R
- Rabbit ear mange preparation, 185  
Rancidity-preventing agent, 151  
Rat poison, 127  
Reactivity of glycerin, 5  
Refining of glycerin. *See* Purification.  
Remoistening adhesives, 11, 12  
Rennet, alcohol-glycerin, 151  
Resin, alkyd, 27, 73, 81, 82, 95, 98, 108,  
109, 119, 174, 193  
— glyptal, 27, 73  
— lubricant, synthetic, 48  
— plasticizer, polyvinyl, 101  
— roller, synthetic, 91  
Resins, classification of alkyd, 97  
— history of alkyd, 96  
— manufacturers of alkyd, 98  
— production of alkyd, 97  
— properties of alkyd, 96  
Resist, 106  
Restrainer, photographic, glycerin as,  
74  
Retained afterbirth wash, 187  
Ringworm treatment, cattle, 183  
Roller, coated, 90  
— composition, 88, 90  
— “non-meltable,” 90  
— rubber, 91  
— spray, 91  
— synthetic resin, 91  
Root canal preparation, 167  
Rubber, 99  
— coating, synthetic, 110  
— conservation, 102  
— finish, synthetic, 99, 100  
— latex softening agent, 99  
— lubricant, 46  
— preservative, vulcanized, 173  
Rubber roller, 91  
— substitute, 103  
— surface coating, 100  
— surface lubricant, 101, 102  
Rust remover, 53
- Safety glass, 119  
— glass laminating agent, 195  
Sand, molding, 171  
Saponification of fat, 2, 3  
— of oil, 2  
Sarcoptic mange treatment, 185  
Scale remover, forge, 53  
Scheele, Karl Wilhelm, 1, 2  
Scrap-tobacco flavoring composition,  
116  
Screen printing, 93, 105  
— projection, 79  
Sealing composition, container, 84  
— composition, composite container,  
12, 13  
— composition, food container, 100  
Seasoning agent, 154  
Seed germination, 124  
Shampoo, dog, 185  
Shaving preparation, 137  
Sheep dip, 128, 190  
— dip, “Carbolic and Glycerine,” 190  
— myrris, 183  
Sheet, abrasive, 84  
Shortening, 150  
— plastic, 150  
Silver polish, 20  
— polishing cloth, 20  
Size, beater, 69  
Sizing agent, paper, 66  
— agent, textile, 106  
Skin cream base, matt, 132  
— disease, 159  
Smokeless powder, 32, 35  
Soap lyes, glycerin from spent, 2  
Sobrero, Ascanio, 31  
Sodium alginate solution, glycerin in,  
131  
Softening agent. *See also* Plasticizer.  
— agent, hide, 37, 38  
— agent in the tobacco industry, 114  
— agent, paper, 65  
— agent, paper napkin, 66  
— agent, paper towel, 66

